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A technical investigation of an oil painting on copper support, including a study on consolidants for treatment

Dissertação para obtenção do Grau de Mestre em
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Resumo

Esta tese divide-se em duas partes. A Parte 1 foca-se no estudo técnico de uma pintura a óleo sobre cobre não datada. A pintura, que representa a cena bíblica "*A Visitação*", chegou ao laboratório em mau estado de conservação, com graves destacamentos activos que originaram perdas de tinta extensivas.

A Parte 2 investiga a gama de consolidantes disponíveis para tratamento de destacamentos de tinta, descrevendo as experiências levadas a cabo para determinar a adequação de uma selecção dos mesmos. A literatura sobre pinturas a óleo sobre cobre e acerca dos consolidantes usados no seu tratamento é escassa. Com base nos poucos artigos existentes, foi efectuado um projecto-piloto empírico sobre os seguintes polímeros sintéticos: Paraloid B-67, Paraloid B-44, Regalrez 1094, Paraloid B-72, Mowilith 20, Beva 371b, e Laropal A 81. Destes, foram seleccionados os últimos quatro para uma investigação mais detalhada, focada na sua interacção com cobre, especificamente sobre a difusão de iões de cobre nas matrizes poliméricas. Este é um tópico de interesse dado estar descrita, na bibliografia, a acção catalisadora de partículas metálicas em processos de degradação de polímeros.

A Espectroscopia de Retrodispersão de Rutherford (RBS) foi escolhida para investigar este assunto, numa série de cupões de cobre revestidos com os quatro polímeros. Devido a danos nestes revestimentos causados pelo feixe de RBS durante a análise, os resultados foram inconclusivos. Recorreu-se ao SEM/EDS para complementar a informação dada pelo RBS, mas não foi detectada a presença de cobre em amostras dos mesmos revestimentos, indicando ou que estes polímeros e o cobre não interagem, ou que o tempo de envelhecimento acelerado das amostras adoptado foi demasiado curto.

Ainda assim, o estudo dos materiais da pintura, na Parte 1 conseguiu estabelecer com sucesso um período de datação para a pintura, e obter novas percepções acerca de substâncias que parecem resultar da interacção entre o suporte de cobre e as camadas pictóricas.

Palavras-chave: pintura a óleo sobre cobre; consolidantes; resinas sintéticas; difusão de cobre

Divulgação do trabalho:

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Abstract

This thesis is divided into two parts. Part 1 focuses on the technical study of an undated oil painting on copper. The painting, which depicts the Biblical scene *'The Visitation'*, arrived at the laboratory in poor condition, with severe active flaking which has resulted in extensive paint losses.

Part 2 investigates the range of consolidants available to treat flaking paint, and the experiments carried out to determine the suitability of a selection of these. The literature on oil paintings on copper and on consolidants used in their treatment is scarce. Based on the few articles that exist, an empirical pilot study was made of the following synthetic polymers: Paraloid B-67, Paraloid B-44, Regalrez 1094, Paraloid B-72, Mowilith 20, Beva 371b, and Laropal A 81. From these, the last four were selected for a more detailed investigation focused on their interaction with copper, specifically concerning the diffusion of copper ions into the polymeric matrices. This is a topic of interest due to descriptions in the literature of metal particles acting as catalysts in polymer degradation processes.

Rutherford Backscattering Spectroscopy (RBS) was chosen to investigate this subject on a series of copper coupons coated with the four polymers. Due to beam damage of the coatings during analysis, the results were inconclusive. SEM/EDS was used to complement the information from RBS, but did not detect the presence of copper in samples from the same films, either indicating that these polymers and copper do not interact; or that the time for the accelerated ageing of the samples was too short.

Nonetheless, the material study of the painting in Part 1 successfully established a date range for the painting, and new insights into substances which appear to result from interactions between the copper support and the pictorial layers were found.

Keywords: oil painting on copper; consolidants; synthetic resins; copper diffusion

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List of Symbols and Abbreviations

UV	Ultraviolet Light
IR	Infrared Light
OM	Optical Microscopy/Optical Microscope
μ-EDXRF	Micro-Energy Dispersive X-ray Fluorescence Spectroscopy
μ-Raman	Micro-Raman Spectroscopy
μ-FTIR	Micro-Fourier Transform Infrared Spectroscopy
PIXE	Particle Induced X-ray Emission
SEM/EDS	Scanning Electron Microscopy with Energy Dispersive Spectroscopy
RBS	Rutherford Backscattering Spectroscopy
T_g	Glass Transition Temperature
T	Temperature
RH	Relative Humidity
MeV	Megaelectron-volt
nA	Nanoampere
at/cm^2	Atoms per centimetre square
BA	Butyl acrylate
EA	Ethyl acrylate
MA	Methyl acrylate
BMA	Butyl methacrylate
iBMA	Iso-butyl methacrylate
EMA	Ethyl methacrylate
MMA	Methyl methacrylate
VA	Vinyl acetate
PVA	Poly(vinyl acetate)
EVA	Ethylene-vinyl acetate

PART 1

1. Introduction

1.1. Description & visual interpretation of the painting

The subject depicted in this painting is a religious one, belonging to the Bible's New Testament, and known as '*The Visitation*' [1]. It is one of the scenes from the *Life of the Virgin*, where Mary, then expecting Jesus, (see Fig. 1, third character from the left in the foreground group) travels to her older cousin Elizabeth's house to visit her (see Fig. 1, fourth character from the left) after knowing she was also expecting a child. When the two greet, Elizabeth is filled with the Holy Spirit brought by the unborn Jesus, and her child, John the Baptist, leaps with joy in her womb. Mary, accompanied by her spouse Joseph (see Fig. 1, second character from the left), seems to have travelled by donkey, for its two hind legs are visible behind the first figure from the left, which is a maid (see Fig. 2 a & b). Zachariah, Elizabeth's husband, is also seen at the entrance to his house (see Fig. 2 c & d). This painting's style of representation, with an impressive amount of well executed minute details filling the whole composition, is thought to be Flemish (16th/17th century)[2].

Figure 1 – Overall before treatment photograph of *Visitation* in normal light.

(a) (b) (c) (d)

Figure 2 –Detail of the maid: (a) normal light; (b) in infrared (IR). Detail of Zachariah: (c) normal light; (d) IR.

All three figures (Mary, Joseph, and Elizabeth) are depicted plainly, without halos, and dressed in traditional costumes. On the other hand, both the maid and Zachariah are dressed with garments belonging to a certain epoch (see Fig. 2 a–d), determined to be the second half of the 16th century by costume experts Dr. Xénia Ribeiro and Dr. Dina Dimas[3]. For the maid, indicators are her dress with a high waistline; the veil which covers her head partially; and her hair style. As for Zachariah, features

[1] Holy Bible, New Testament, Gospel of St. Luke, Chapter 1, verses 39–45.
[2] Personal communication, Art Historian, Dr. José Manuel Ferrão, October 2014. This conclusion derives from a preliminary evaluation of the painting from the Art History point of view. A further in-depth study will be carried out.
[3] Personal communication, Dr. Xénia Ribeiro and Dr. Dina Dimas, August 2015.

include his long coat with wide sleeves; his high stockings; and his beard style. The proposed dating has, however, some reservations, due to these costumes being popular ones, therefore not having changed as much throughout the years as the ones from the middle and upper classes.

1.2. Historical context – Copper as a support for paintings: development & technology

The practice of painting on metal surfaces with the aim of producing art has been around since ancient times [1]. Painting on copper supports has been attractive to artists for a variety of reasons of both a practical and an aesthetic nature, detailed below:

- According to Horovitz [2], they are expected to be more durable than paintings on canvas or wood, due to the support being rigid (thus, not being susceptible to tearing or cracking), and due to being made from metal, which does not suffer from biological attack nor does it exhibit a strong response to fluctuations of temperature and relative humidity (as organic materials do), but only from minor dimensional changes due to temperature (in normal indoor conditions). Such features account for the surprisingly good state of preservation that some paintings exhibit still today. Bowron [3] notes that the rigidity of the support, added to their usually small format, contributed greatly to their portability (allowing, for example, the collaboration of two painters residing in different places on the same painting, and easy circulation in the art trading circuits).
- As noted by Horovitz [2] and Bowron [3], the act of preparing the copper plates to receive the pictorial layers is consistently reported in historical treatises and manuscripts to be easy and simple (as discussed below);
- They can offer extremely smooth surfaces, which allowed artists to paint with fine detail and delicacy at very small scales, using small brushes [2; 3];
- Horovitz [2] states that because copper supports are non-absorbent, colours can remain rich and highly saturated, even if applied in very thin layers/glazes, due to the oil binder not being absorbed to a great extent. She notes that this could have resulted in an economical use of pigments [2].
- Both Horovitz [2] and Bowron [3] state that the metal substrate provided a reflective support. This, in combination with the abovementioned smoothness, non-absorbency, and application of thin paint layers resulted in paintings with a very unique, translucent and luminous look, almost '…three-dimensional…' [2, p. 78] and often described as '…jewel-like…' [3, p. 10], which is said to exist even when artists applied thin preparatory layers to cover the copper [2].

1.2.1. Emergence and development

Based on documentary sources produced by artists using the technique, oil paintings on copper can be traced back to the first half of the 16th century in Italy [3]. The earliest surviving paintings attributed to named artists date from the second half of the same century, around the 1560's and 1570's [3]. According to Bowron [3], paintings on copper seem to then have had a peak of popularity and production in Europe (mainly Italy and Northern countries Germany, Netherlands and Flanders) from around the second half of the 16th century to the second half of the 17th century; and from then on they went into decline, which lasted up until the 18th century.

The precise reasons which led to the adoption of oil paintings on copper are not fully understood [1]. However, attempts have been made to explain their popularity which are based on historical evidence linked to artistic tradition and to both the socio-cultural and economic context, which may help to elucidate this subject.

Concerning artistic tradition, there are three main artistic techniques, all predecessors of oil paintings on copper, which are thought to may have played an important role in its emergence:

- As Horovitz [2] relates, paintings on copper may have arisen out of an older practice of applying oil in the form of translucid glazes to metal foils[4];
- The practice of translucent enamelling on copper or bronze, which is known to have been mainly developed in Limoges, France, in the course of the 15th century [2; 4] may have influenced its development, due to their widespread popularity [4].
- The practice of engraving and etching, also widely popular in Europe during the 15th/16th century meant that there was a greater availability of ready-made (cut) copper plates [2]. In addition, it is also reported that some painters were also etchers and engravers simultaneously [2].

Aside from availability, economy is also thought to have played a role in the development of this kind of artwork, in the sense that an increased availability of copper plates meant a reduced cost, a factor that must have contributed to their purchasing at a greater extent by painters [3]. Investigations carried by Wadum [5] showed that, at that time, the price of a copper plate compared to that of an oak panel of comparable size was not much different.

At a socio-cultural level, Bowron [3] notes that in the late 16th century Europe there was a predominant climate of '…appreciation for the precious and the remarkable, the rare and unusual, the refined and exquisite…' [3, p. 11], typical of the high-class humanistic circles and much reflected in the *Kunstkammer* (cabinets of curiosities). As a result, a number of unusual supports for paintings, such as '…alabaster, amethyst, lapis lazuli, marble, quartz, slate…*pietra paesina*…tortoiseshell…' [3, p. 11] and, of course, metal, emerged at that time. Thus, copper fell into this category, and paintings on copper were consequently seen as '…rare and precious…' [3, p. 11] objects which were integrated into the most refined art collections.

The progressive disappearance of the production of oil paintings on copper from the second half of the 17th century onwards in Italy and the Netherlands is even less understood than their appearance, and no reasons for it have yet been given [3]. On the other hand, countries such as France and Spain increasingly admired this kind of artwork throughout the 18th century, and many of their artists chose copper as the main support for their paintings [3].

[4] The earliest known documented evidence of this is found in the 8th century "*Lucca Manuscript"* [2-4], where a recipe on how to make a glaze from oil and resin to be applied over tinfoil is given, in a technique known as '*Pictura translucida'*, for the glazes could be coloured yellow to stain the tin with the aim of imitating gold leaf [2]. Other sources posterior to this one discuss paintings on different metal substrates [2].

1.2.2. Materials and technology

1.2.2.1. Manufacture of the copper plate

According to Wadum [5] the manufacturing process of copper plates was already well established by the 15th/16th century, as a result of the demands of high production of the newly-emerged printing industry. Horovitz [1; 2] describes such process, which is summarised here: cast ingots (slabs or sheets) were made from melting the copper alloy and pouring it onto an inclined bed of sand (mould); where they were left to cool until the metal solidified. The ingots then went through a beating process, using hammers usually powered by water, to decrease their thickness while forming them into larger sheets (according to the size of the initial ingot, and the desired thickness). The sheets were then cut into smaller pieces using water-powered shears, and could be beaten again to decrease their flexibility, for heavily worked metal becomes less plastic and more resistant to mechanical deformations than less worked metal.

Once made, the sheet could be flattened further by hand using a planishing hammer which, if used with skill, can flatten only the surface of the sheet without causing any substantial deformations to it. An alternative method to flatten the sheets was the use of rolling mills. Horovitz [2] reports that the first known rolling machines are depicted in Leonardo Da Vinci's 15th/16th century *Codex Atlanticus,* with other models being represented in 17th century treatises, and notes that such machinery was probably used only for small-scale adjustments, and not for the mass production of copper sheets (since this involved a significant decrease of thickness). According to Horovitz (writing in 1999) it is believed that rolling machines only became more widespread in Europe and were technically improved from the 18th century onwards, and that consequently the majority of copper supports for oil paintings from before this time was most likely flattened by hammering. She notes that there is also the possibility that copper plates (probably prior to the 18th century) received a combination of machine and hand hammering**.**

1.2.2.2. Preparation of the copper plate to receive pictorial layers

Artists were conscious that copper plates required special preparation in order for the pictorial layers to adhere well. As noted by Horovitz [1; 2], this preparation usually started by roughening the copper surface, to '…provide a tooth for the application of the paint…' through the creation of grooves [2, p. 68]. This mechanical action would remove the naturally-created layer of cuprite (CuO_2) from the surface of the plate, leading to an increase of '…the surface area available for bonding, to accept the paint…' [2, p. 68]. The methods employed and recommendations for this step are described in a number of historical treatises and manuscripts[5], and include rubbing the plate with materials such as ashes and pumice stone [1].

Some of the same historical records also refer to the application of garlic, either by rubbing directly a cut clove onto the copper surface, or by coating the surface with strained garlic juice [2]. According to Horovitz [2], once applied to the metal, it provides a sticky base coating, and for this

[5] A literature review of these has been done by Horovitz [2], Stols-Witlox [7], and more recently by Vega [8], in a student's project carried out in 2015 at the DCR FCT-UNL. Vega has added a new reference to the ones present in Horovitz's and Stols-Witlox's reviews (see Vega Project Report [8]).

reason it not only provides some 'tooth' for the subsequent pictorial layers, but also gives the artist a better control during the application of the painting preparation layers. She also refers that garlic is reported to have been applied with the aim of filling uneven areas of the support, therefore making it more uniform.

Horovitz [2] notes that coating the copper surface with turpentine (instead of garlic) is also reported in some sources, and is justified to improve the wettability of the smooth, slippery copper surface, helping the oil applied on top to penetrate.

Horovitz [1] and Stock [6] both mention another practice for the copper plate preparation, which is to apply a layer of linseed oil. They note that this could be done in order to clean the surface from any residues of substances used to roughen the plate, being a practice borrowed from etchers; or as Stock [6] notes, for practical purposes, as its presence is thought to facilitate the subsequent application of the preparation layers. Stock also links, though with reservations, the presence of this oil layer to the etchers' practice of applying a special ground, known as a 'hard ground', consisting of linseed oil and colophony, prior to etching.

Horovitz [2] also notes the practice of using tin coated copper plates (these are sometimes seen). She states that their adoption may be aesthetic, since it provides a highly reflective surface that would result in paintings with an '…incredible luminosity…' [2, p. 68]; furthermore the tinned surface would protect the copper from corroding.

1.2.2.3. Application of the preparatory layer

Horovitz [2] reports that the majority of oil paintings on copper she has studied exhibit a '…thin, pale-toned preparatory layer …' [2, p. 71], almost always covering the support completely. Vega [8] has summarized the information found in the same aforementioned historical sources about preparatory layers for paintings on copper, according to the colours (pigments) that are mentioned, and to the different methods of application. The materials he lists are: lead white; white or green ashes; black coal; umber; yellow ochre; *tierra roja* (red ochre); and vermillion. He notes that some authors also refer to undetermined "light colours". According to Horovitz [2], these materials were ground in oil; Vega [8] also concludes this, since the sources either mention it explicitly, or suggest its use by placing the descriptions in chapters dedicated to oil painting[6]. The techniques mentioned for applying the ground vary between using the palm of the hand; using the fingertips; and brushing [2; 8], the first one being the most frequently referred in the sources [8].

[6] Oil painting manuals describe a variety of ground preparations aside from pigments bound in oil (glue, paste, etc.). Since the use of anything that is aqueous-based is not recommended for copper due to the promotion of corrosion; this would explain a preference for oil binder in ground layers for paintings on copper. Thanks are due to Dr. Carlyle for this observation.

2. Condition report

Condition Summary

Visitation exhibits significant active flaking paint problem, mainly evident in darker areas of paint, which has resulted in several paint losses spread throughout the painting. For this reason, it is considered to be in a poor, unstable condition. It probably has been in this condition for some time, due to evidence of having the pictorial layers extensively restored. The same darker areas display significant differences in terms of texture by comparison with the remaining colours, being much textured and exhibiting several “lumps”, while the others are considerably smoother.
Three different substances were observed at the interface between the copper support and the preparatory layer, which are thought to be products resulting from interactions between the two, these are described in detail below.

2.1. Painting support

The two upper corners of the copper plate exhibit out-of-plane undulations: in the upper left corner, damage originated from the left side of the plate; and in the upper right corner, coming from the top diagonally. The deformations might have happened in the process of framing, although the current frame is quite loose-fitting and none of the edges of the copper plate, with the exception of the bottom one, were in contact with the wood when the painting first arrived in the department. The deformation of the left corner is more severe than the one on the right, and because of that it resulted in a paint-loss of considerable size (approx. 3.5cm x 2.5cm) (see Appendix III, Map of damages); no paint delamination occurred on the right corner.

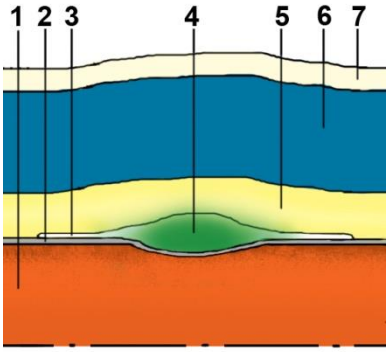
Both surfaces of the copper plate – the front surface being visible through paint loss areas – are oxidized, resulting in an overall tarnished and stained appearance; and exhibit localized vivid green copper corrosion products, either in the form of small-sized, rounded crusts (ranging between approx. 0.5-5mm) or as thinner layers (see Appendix II, Fig. II.1). Based on appearance and the reactions copper is known to have with moisture and the surrounding atmosphere, the oxidation layers form, under dry, unpolluted conditions, what is usually a protective patina, and are expected to be a mixture of cuprite (Cu_2O) and tenorite (CuO). In the presence of carbon, sulphur and chlorine ions from the atmosphere, corrosion products may be either copper carbonates (such as malachite - $CuCO_3.Cu(OH)_2$); copper sulphates (as antlerite - $CuSO_4.2Cu(OH)_2$ - and brochantite - $CuSO_4.3Cu(OH)_2$); and/or copper chlorides (atacamite and paratacamite - $Cu_2Cl(OH)_3$) [9; 13; 11].

The back surface of the plate (see Appendix I, Fig. I.2) also displays varnish drips coming from the edges; splashes of a white substance that is known to be wall paint, according to the owner; and concreted dirt in the form of localized crusts.

White-grey layer & white powdered substance

Also covering unevenly the front surface of the plate, being more evident in some areas than others, there seems to be a very thin, translucent layer of an unknown substance, matte and white-grey in colour (see Appendix II, Fig. II.2-II.3). This layer was observed under the stereomicroscope in

both old and newer micro-paint-loss areas (created upon the collection of micro paint samples to do cross-sections, and due to the composite being currently actively flaking, when the painting arrived into the lab), which suggests that it may be present underneath the painting as well and possibly covering much of the copper plate. By scraping this layer very gently under the microscope using a micro-tool, it was found to be similar in consistency to wax: very soft and easily removable by mechanical action, along with the layers of copper oxides (see proposed stratigraphy in Fig. 3), revealing the shining copper substrate underneath. Its colour may be a characteristic of the substance itself, or a chromatic alteration that has happened over time either due to chemical reactions within the substance or with its surroundings, including the accumulation of dust and dirt.



1 - Copper plate (support)
2 - White-grey layer
3 - Transparent interfacial layer
4 - Green translucent interfacial layer
5 - Ground layer
6 - Paint layer
7 - Varnish layer

Figure 3 – Proposed stratigraphy.

Due to the pictorial layers and the copper support having been in direct and prolonged contact, this layer may be the reaction product of a chemical interaction between the organic media and/or certain pigments belonging to the paint composite (preparation layers, paint) and the copper. It could also represent vestiges of a particular substance that has been used or applied to the copper plate as part of its preparation prior to painting (mentioned above in 1.2.2.2); or an organic layer applied to both sides of the copper plate to prevent oxidation that the artist who painted *Visitation* thought suitable to use.

Alongside this layer, a white powdered loose substance was also noticed in every paint loss area, being deposited on the copper support as well (see Appendix II, II.2-II.3). It appears to be mainly concentrated near the paint losses' edges, and is more evident in smaller paint losses than in larger (in the latter case it has probably been eroded due to a larger portion of the copper being exposed to the outside environment). Similarly to the white-grey layer, it is very easily removable by mechanical action. It was also seen on top of the paint composite, mixed with regular dust and other deposits, though not as abundantly. The reasons for its presence are still unclear at this point and need further investigation, although one possibility is that it is residue of the ground layer that has crumbled during delamination of the paint composite.

2.2. Preparation layer

The preparation layer of the painting is very thin; light coloured; and barely noticeable when looking at the painting under the microscope.

It is considered to be in good condition, but exhibiting a very low level of adhesion to the copper support due to the significant amount of paint losses the painting exhibits, apparently deriving from interlaminar cleavage happening at the copper/ground layer interface.

Observation under the optical microscope of the underside of several paint flakes that got detached from the copper support during handling of the painting, contributed to a better

understanding of some interfacial phenomena discussed in the literature concerning oil paintings on copper [1; 2; 4; 6; 10-14]. Three substances were observed, each with specific features:

1. A very thin, translucent green layer, showing no signs of individual particles, is found coating unevenly the bottom of the ground layer, immediately above the copper plate (see proposed stratigraphy in Fig. 3). It appears more concentrated in some areas and less – or nothing – in others (varying between 1.5μm–6μm, according to cross-sections evidence) (see Appendix II, Fig. II.4 and II.5). This unevenness may be due to the fact that, as mentioned further in Section 3, the copper plate was scored and sanded before paint application, therefore having grooves in which this layer may have been more prone to grow. Visual evidence suggests that this substance does not usually behave like an independent layer from the ground, for it seems to be tinting the preparatory layer in the places where it starts to appear. A variation in colour saturation is visible (in cross sections and on the back of paint losses where it sits directly on top of the ground), ranging from a paler, more translucent green, to a richer, denser one – an aspect that seems to be directly related to the layer thickness (thicker meaning denser and greener, and vice versa). An increase in thickness, associated with bigger areas, also seems to be related to the appearance of micro fissures, indicative of a fragility and lack of internal cohesion in the material. This layer does not fluoresce in UV (Pavlopoulou [15] reported a similar layer between the ground and a copper substrate on an oil painting, also non-fluorescent in UV).

A similar layer by description and photographic evidence has been reported in the literature, and is thought to be a common characteristic of all oil paintings on copper [1; 2; 4; 6; 10-14]. Authors [1; 2; 4; 6; 10-14] agree that this layer is composed of copper carboxylates, derived from a reaction between the copper ions of the support and the carboxylic acid groups of the paint medium (drying oils), together with acidic degradation products during paint ageing (mainly by oxidation and hydrolysis) [11]. This compound has been confirmed through scientific investigations [2; 11; 16–18], where copper carboxylates and organometallic copper complexes have been successfully identified, mainly by μ-FTIR analysis. Daniel Vega has carried out a project this year in the DCR-FCT paintings lab, where the preparatory layers from twelve different oil paintings on copper showed the same green layer in cross-sections observed under the OM[7].

It is yet to be understood whether this layer is formed by the prolonged contact of the oils belonging to the paint media with the copper, or to a deliberately applied layer of oil before beginning the painting process, to ease the application of paint [2; 6]. In the latter case, empirical tests carried out by Horovitz [1], where different kinds of drying oils were applied to copper strips, revealed the appearance of green discolorations within a period between 24 hours to 10 days. Other possibilities could be the reaction of the oil and/or copper with contaminations of materials used to clean the plate [2]; or the use of garlic to prepare the plate to receive the paint layers could also react with the copper, forming green compounds (this last phenomenon has been proved in empirical tests carried out by Horovitz [2]).

The role of the green layer regarding promoting the adhesion between the copper plate and the ground layers or the promotion of flaking is not clear. Van de Graaf [4] has suggested that its presence

[7] Personal communication, Daniel Vega, June 2015.

helps the adhesion of the ground to the support, however in *Visitation* paint fragments which are already detached bear evidence of the green layer attached to the underside, leaving no traces behind in the copper support which suggests that it may promote detachment, at least in this painting [14]. Although the flaking of paint may be caused by a number of other factors, this may demonstrate that the existence of the green layer at the interface between the ground and the plate does not always and necessarily mean excellent adhesion of the paint composite to the support.

2. An extremely thin, transparent and non-particulate, vitreous looking layer has been observed, but not on every paint fragment (see Appendix II, Fig. II.5; II.6 and II.8). It is barely visible with OM with normal reflected light, on the underside of the paint composite (on the bottom of the ground) (see proposed stratigraphy in Fig. 3). Due to its thinness and lack of colour, it is not visible in cross-sections. These features also make it difficult to determine if it is thicker in some areas compared to others, and if it is yellowed or completely clear (due to the ground underneath being coloured). Observations under the OM with UV light and different filters for fluorescence (see instrument description in Appendix IV.1) showed that this substance fluoresces strongly (see Appendix II, Fig. II.5; II.6 and II.8). Because of this, it is possible to determine its location and distribution on the underside of the fragments: similarly to the green layer, it does not coat the ground evenly. It appears either in the form of continuous films and patches. In some areas, at the outside edges, it displays perfectly formed dendritic shapes (see Appendix II, Fig. II.8). Also, it occasionally exhibits a pattern with thin striations. This may be related to its method of growing on the non-porous support or, again, due to the plate possibly being scored and sanded, therefore not being a perfectly smooth surface. Micro-fissures were also detected in this layer in some areas, similar in appearance to those found in the green layer. This transparent layer sometimes appears together with the green one on the underside of the ground in paint fragments, but it was difficult to determine if it is on top of the green, or if it is a continuation of it on the sides, and if the two are merged with each other or separate. One possibility is that they are the same substance, and the presence or absence of colour is due to the layer thickness or a concentration of copper ions (the green areas having a higher concentration of copper).

References in the literature to a non-green interfacial layer in oil paintings on copper are very few, however there are descriptions: Richard Buck reported an '…organic pellicle, now rather yellowed, between the metal and the paint…' [19, p. 25] and while observing a copper plate covered with tin alloy; Horovitz reports findings by Aviva Burnstock of a '…translucent layer that was not green…' [2, p. 90] in an uncoated copper support (with no tin layer). Pavlopoulou & Watkinson talk about a …transparent and non-particulate…' [11, p. 58] layer at the interface between copper and ground.

3. A significantly thicker, vivid green layer was observed on only one paint fragment thus far (see Appendix II, Fig. II.7). Its thickness has not been measured due to the fragment not being in cross-section. It appears to be on top of the paler green, thinner one described above (most commonly found), but it is not clear if the first is an evolution of the second. Like the green layer, it does not fluoresce under UV light, and it does not coat the underside of the fragment evenly. But unlike the green layer above some of it was left behind on the copper surface when the fragment was collected, indicating that the substance can fracture within the layer itself (lack of internal cohesion), and

suggesting that it has greater adhesion to the copper support, at least in places. Also, using higher magnifications, it is possible to see that it has some texture and is not as clear as the green layer above.

Horovitz distinguishes and warns not to confuse corrosion products related to the copper support with products originating from an interaction of the organic paint binder with the copper (resulting in a copper carboxylate layer) [10]; but it is Paquette [14], discussing the results of an experiment she carried out, who clearly discriminates two types of green layers at the interface between paint and copper: a '…distinct vivid green layer…' and a '…pale green one, which formed a layer within the ground…' [14, p. 5]. She also reported that '…These two types of corrosion were randomly distributed throughout all the samples…' [14, p. 5] and that '…in most cases, the corrosion layer had separated from the copper plate, but always remained attached to the ground layer. In some cases, the corrosion layer had split in two: one part remaining attached to the ground layer and the other adhered to the copper plate…' [14, p. 5]. The observations of the paint fragments belonging to *Visitation* are very similar to Paquette's. The fact that this layer was sandwiched between the ground and the copper suggests that it is an interfacial layer formed following the same mechanism described for the other green layer above. However this does not explain why it is so different in appearance.

2.3. Pictorial layers

The most striking feature of this painting regarding its condition is the drastic difference in the state of the paint between darker colour areas (primarily in the foliage) and the remaining colours (blues, greens, beiges/browns, flesh tones, and reds). In every area where the paint is currently dark (it is unclear whether it has undergone change, or was very dark to begin with) severe mechanical cracking with associated flaking is observed. In these areas the paint islands resulting from mechanical cracking exhibit an extremely low level of adhesion to the support, are very brittle, and are slightly cupped (see Appendix II, Fig. II.9). It is also very "lumpy" in terms of texture; it has a high concentration of small vivid green circles protruding at the surface (see Appendix II, Fig. II.10 and II.11), which were later characterized to be composed of atacamite or paratacamite (see Section 3.2), and it seems to have a higher amount of binder (oil) in comparison to the other colours, as this was evident in cross-section under the microscope (see Appendix IV.3, Fig. IV.6).

A higher binder ratio makes sense in the context of darker-coloured paints [20], and may offer an explanation for the poor condition of such paint areas: more oil means more shrinkage when the paint is drying, and this creates internal stresses that ultimately may result in a higher amount and extent of "shrinkage cracks". The strength of such stresses created in the top layers, together with a good level of bonding between them and the ground, may have been enough to crack the paint composite all the away to the support – thus explaining why the only kind of interlaminar cleavage this painting presents is the one happening at the copper/ground interface [8].

The "lumpy" texture may be due to either poorly ground pigment particles, or to the presence of the aforementioned green protrusions, for in most cases where they appear, the surrounding paint

[8] Thanks are due to Dr. Carlyle and Dr. Isabel Pombo Cardoso for this useful discussion.

seems to be slightly pushed up, creating that visual effect. It is also important to mention that the green circles were also observed in other colour areas, but less frequently.

There is a deposit of a substantial amount of dust and other particulates over the whole surface. In some areas the paint is wrinkled, which is not unexpected for paint applied on a non-porous substrate, such as copper [1]. However, in general the paint in the remaining colours (blues, greens, beiges/browns, flesh tones, and reds) appears to be in good condition, smooth and in plane, with no significant mechanical or drying cracks.

2.3.1. Previous surface treatments

This painting is extensively restored by more than one hand, indicating a history flaking (see Appendix III, Map of damages). The restorations appear to be restricted to surface treatments as there is no visual evidence of previous consolidants, other than where oil paint appears to have been used to adhere the edges of losses in areas of overpaint. Treatments are essentially infills with overpaints as well as inpainting of previous paint losses, together with a new varnish layer (see evidence in Appendix IV.3, Fig. IV.2 and IV.7).

The overall appearance of most fills and retouching areas is not satisfactory, since most of them are quite distinguishable from the surroundings, mainly because both texture and colour do not match, or due to their being in a lower level than the paint surface. Both infills and inpaintings appear to be oil based with some inpaintings glaze-like and translucent, allowing the copper to be visible shining through from below. Some of the retouching areas exhibit a wrinkled surface, but all appear to be secure, since none is apparently cracked or actively flaking off.

An attentive observation and comparison of the previous restorations suggested that they were probably done by at least two different hands (maybe in two different restoration campaigns), due to their appearance being sometimes very different.

Observation of the painting under IR light showed that some previous reintegrations appear black, indicating the presence of a carbonaceous material in such locations (see Appendix I, Fig. I.6).

2.4. Surface coating: varnish

The current top varnish layer on the painting is thought to have been applied during a restoration campaign due to evidence in cross-section S1 (see Section 3), where there is an overpaint layer between two layers of varnish, the bottom of which covers the original paint layer. It is a thick layer, significantly yellowed (in part due to its nature: a triterpenoid resin – mastic or dammar –, confirmed by μ-FTIR analysis, see spectrum in Appendix IV.6, Fig. IV.17), and with an apparently even gloss (although partly hindered by the large amount of dust and dirt deposited on top).

Observation under ultraviolet light (UV) indicates that it was applied over the entire surface (not stopping at the frame edges) (see Appendix I, Fig. I.5). It was not an even, smooth application, for build-up lines that mark the beginning and the end of the brushstrokes and some slight pooling areas, and some overlaps of varnish layers are quite evident. Observing the direction of the brushstrokes and noticing the absence of vertical varnish drip lines indicate that the painting was likely varnished while horizontal.

Under close observation, and especially with raking light, it is possible to see that the varnish layer has an independent crack pattern from the paint. The pattern varies both in density and orientation, which appears to depend on the way the varnish was applied with a brush. Crack lines are always sharp-edged, and varnish islands are very close together. While collecting varnish samples for μ-FTIR analysis, it was evident that the varnish is very brittle and easily detachable from the paint layer underneath.

The yellowing of the varnish is especially evident where the varnish is thickest, such as where excess has pooled to forms lines, and in the areas over lighter colours.

3. Characterization of materials & techniques

3.1. Analysis of artistic techniques

3.1.1. Copper support

According to the methods of production of copper plates described in Section 1, observation of the painting under raking light suggests that the plate was flattened by hammering after being cast. This is because there is a discrete overall undulated appearance, with concave areas. These deformations are not visible with normal light, but become very evident with raking light (see Appendix I, Fig.I.3 and I.4).

Although this evidence cannot lead to precise dating, it can help in the sense that, according to Horovitz, "…until well into the eighteenth century, hammering was the main method of manufacture…" [2, p. 66] of copper plates, until the introduction in the 18th century of rolling machines (see Section 1).

Because of the extremely loose paint on the surface of the plate, it has not been possible to carry out X-radiography and ultimately a metallographic examination, where the crystalline microstructure of the copper alloy is observed under an optical and/or electron microscope. Both methods will help to elucidate the manufacturing process, the first by giving information about variations in metal density related to uneven thickness of the plate (thus producing identifiable patterns); and the latter by showing the type and organization of the metallic grains present.

The plate has irregular dimensions and edges, indicating that it was not cut very carefully. The edges seem to have been filed, for diagonal, regular grooves can be seen in the thickness of the plate under the stereomicroscope with high magnification. The front surface appears to have been roughened or scored, probably to attain better tooth to receive paint (see Section 1). This has resulted in an uneven and random pattern of scratches, clearly visible in some areas (under high magnification), while barely evident in others.

Overall, this copper plate offers a smooth and flat surface that must have been suitable for the painter to paint this scene in particular, filled with small scale details and, in some areas, using very fine brushstrokes.

3.1.2. Painting technique

As stated by Horovitz, "…in a painting on copper, build-up of paint layers can be observed when the surface catches the light, producing a sculptured relief effect of the forms in the painting…" [2, p. 76]. As she explains, this is due to the support underneath being non-porous, and excess paint not being absorbed [2]. This is quite evident in *Visitation*, especially when observed with raking light (see Appendix I, Fig. I.3 and I.4). Using this method to examine the painting also reveals that some major forms of the composition were delineated, apparently according to the dominant compositional areas (the hill in the background behind the characters is clearly delineated from the sky, for example). Across the whole painting it is also possible to observe evidence of paint layering, either thinly applied or as *impasto*.

Cross-sections show that the preparatory layer is always a single, very thin application (varying between 12 μm–25 μm in thickness), having light beige as the dominant colour (see Appendix IV.3,

cross-sections S1-S5). In most cases (see Appendix IV.3, cross-sections S2; S4 S5), there is a single layer of paint on top; and in others (see Appendix IV.3, cross-section S5), two layers of paint (particularly distinguishable under Filter F5 for fluorescence), the bottom one being darker, and the upper lighter. In cross-section S1, there is a green overpaint layer that is sandwiched between two layers of varnish (with a final layer of varnish at the surface of the painting, applied after the overpainting).

3.2. Materials analysis

Complementary analytical techniques (see Table IV.1 in Appendix IV) were used to investigate the painting's materials, with the aim of achieving an approximate date of execution and to understand some of degradation phenomena taking place. Tables IV.3 and IV.4 in Appendix IV.4 provide the results of the pigments identified in the ground and paint layers, respectively.

Investigation began with μ-EDXRF analysis of the copper plate, performed on its front side, in paint-loss areas (this orientation was necessary due to the poor adhesion of paint as noted above in Section 2, Condition Report). All the resulting spectra (see one in Appendix IV.8, Fig. IV.25) exhibit, as expected, two intense peaks of copper (Cu Kα; Cu Kβ), and also minor peaks of nickel (Ni Kα) and lead (Pb Lα; Pb Lβ). The presence of nickel could suggest either that the plate was made from a cupronickel alloy [21; 22], or that it contains a trace impurity of this element (e.g. derived from the ore from which the copper was extracted) [13]. As for the presence of lead, it can represent a trace impurity of the alloy as well [13], or it can be a deliberate addition to the alloy to improve its casting properties and machinability [21; 22]. The presence of lead can also be related to contamination from the painting's ground, since it contains lead white (to confirm this last hypothesis, analysis would have to be performed on the back of plate to see if the spectra would still contain lead, but as noted the painting could not be turned over for this step). Quantitative μ-PIXE analysis would provide the exact composition of the copper alloy, but it cannot be performed before the painting is consolidated, since the PIXE instrument available requires the painting to be in a vertical position while being analysed.

Cross-sections of the paint composite were collected and examined using Optical Microscopy (OM) to help understand how the painting was built, i.e., its layering system (see Appendix IV.3, Fig. IV.2–IV.7). The pigments present in the cross-sections were identified using μ-Raman.

All the pigments identified in the preparatory layer (lead white; iron oxides, most likely haematite or goethite; carbon black; and red lead) are consistent with those described in the literature on preparatory layers for oil paintings on copper [2;7], based on information from historical sources (treatises and manuals); and are consistent with the pigments identified by Daniel Vega [8].

Cross-section S4 was collected from an area having one of the green-coloured protrusions frequently found in dark paint areas, (see Section 2 and map in Appendix IV.2). It shows an agglomerate of evenly-sized rounded green particles, which is thought to be a pigment flocculation. Further analysis with μ-PIXE and μ-Raman revealed that the pigment is probably atacamite ($Cu_2Cl(OH)_3$) or paratacamite ($Cu_2(OH)_3Cl$), since the elements Cu and Cl were detected with μ-PIXE, and bands indicative of these pigments appeared in the Raman spectrum (see Appendix IV.4, Table IV.4).

A cross-section from a previous restoration (S6, see Appendix IV.3) was also collected for comparison. It is very different in appearance from the other samples with regard to the ground layer, which, besides being thicker than the original (varying between 45 μm–50 μm), is very homogeneous in terms of texture, has a very pure white colour, and is composed of calcium carbonate and lead white (see Appendix IV.4, Table IV.3). Comparing it to the other cross-section, S2, collected from original paint in the sky area, (see map in Appendix IV.2), it is possible to see that the single blue paint layer present in both varies significantly: in S2 it is considerably thicker than in S6; the size of the pigment particles is much larger in the first than in the latter; and the particles in S2 have a translucent look, whether the ones in S6 seem quite opaque (see Appendix IV.3, Fig. IV.3 and IV.7). Analysis of the pigments with μ-Raman revealed the presence of ultramarine blue in both samples, but S2 contains bands indicative of calcite ($CaCO_3$) whereas S6 does not (see Appendix IV.4, Table IV.4). According to Eastaugh et al, in *Pigmentum* [23], the detection of calcite in this pigment is typically associated with the presence of lazurite, due to both being minerals present in the rock lapis lazuli, from where the so called 'natural ultramarine blue' is extracted. Artificial ultramarine blue, on the other hand, does not usually contain calcite. The fact that calcite Raman bands were detected in S2 (original paint), along with the larger-sized, translucent particles (also typical of natural ultramarine blue [23]) indicates that this pigment in its natural form was used; and that in S6 (restoration) the artificial kind was employed.

Regarding the paint layers, the binder, a drying oil, was characterized with μ-FTIR (see Appendix IV.6, Fig. IV.16). Pigments identified in original paint layers included: lead white; calcite; gypsum; carbon black; lead-tin-antimony yellow; varied iron oxides (ochres); ultramarine blue, probably of natural source; azurite; and atacamite or paratacamite (see Appendix IV.4, Table IV.4). According to Eastaugh et al [23], the period of use for the majority of the pigments found range from Antiquity right up to the present. However, an interesting exception is lead-tin-antimony yellow ($Pb_2SnSbO_{6.5}$). They report that the earliest currently known identification of this pigment in paintings is in the frescos by the school of Raphael, dated from the late 1510s [23]. Alongside the other lead-based artificial yellow pigments[9], its use spread throughout the 17th century in Italy [23], and is reported to decay from the 1750s onwards [23]. The presence of this particular pigment in the painting's original paint layers suggests that it was likely made prior to the late 18th century. As noted above, a stylistic analysis of the painting points to an even earlier period (see Section 1).

The varnish layer was characterized by μ-FTIR and found to be a triterpenoid resin (either mastic or dammar), which helps to explain its extreme yellowing and brittleness previously noted (Section 2) (see Appendix IV.6, Fig. IV.17).

The interfacial translucent green layer found between the copper support and the ground layer (noted in Section 2), was also analysed with μ-FTIR and a copper carboxylate, probably a copper oleate or linoleate was found (see Appendix IV.7, Fig. IV.18). This confirmed analyses reported in the literature [1; 2; 6; 10-14] which were consistent in finding a copper carboxylate.

[9] Lead-tin yellow type I (Pb_2SnO_4); lead-tin yellow type II ($Pb(Sn,Si)O_3$); and lead antimonate yellow (also known as Naples yellow), $Pb_2Sb_2O_7$ [23].

The transparent layer exhibiting dendritic formations which was also found on the underside of some paint fragments (see Section 2) was analysed with SEM/EDS, to investigate the abovementioned theory that it could be the same material as the copper carboxylate, only in a different stage of development. An elemental distribution map was acquired on the underside of one paint fragment containing both transparent and green substances, not covering the ground completely (see Appendix IV.7, Fig. IV.20 and IV.21). The results showed, as expected, a strong presence of lead in the areas free of these layers (due to the ground being mainly composed of lead white); an intense copper signal in the area corresponding to the copper carboxylate, and also a lesser but positive presence of this element in the areas equivalent to the transparent substance (see Appendix IV.7, Fig. IV.21, right). To confirm the latter, spot analyses that gave origin to spectra were performed (see Appendix IV.7, Fig. IV.22-IV.24) Copper was identified in these areas, thus confirming that both layers, the deep green and transparent, might be both copper carboxylate material but with differing copper content. However, only molecular analysis such as μ-FTIR would confirm this completely.

The white-grey waxy layer found as an uneven coating on the surface of the copper plate where it had been in contact with the paint composite (reported in Section 2), was micro-sampled and analysed with μ-FTIR. The spectra show bands indicative of lead white, indicating a contamination from the ground layer, lead soaps, and also different carboxylated substances, still to be further investigated (see Appendix IV.7, Fig. IV.19).

With the aim of understanding interactions between the copper support and the pictorial layers, more specifically processes of copper migration from the first to the latter, additional investigations were carried out using PIXE. Both Broers (2003) [16] and Pavlopoulou (2004) [15] have explored this subject previously through the use of SEM/EDS. Broers analysed a total of five samples[10] through elemental distribution maps alone; and Pavlopoulou the same number of samples[11], but also with X-ray spot analysis (originating spectra), as well as mapping. Broers reports the presence of copper migration only in sample #2 (see footnote 10). Sample #1 showed copper only in the area corresponding to the green copper carboxylates. As Broers noted, '…the migration of the copper ions seems to have been stopped by the lead white ground...', thus implying that it acts as '…a barrier…' [16, p. 44]. In Pavlopoulou's analysis, copper migration was detected in all the samples, to a greater or lesser extent. In her sample #1 (see footnote 11), copper was found to exist not only in significant concentration at the copper/ground interface, in the copper carboxylate areas, but also in the paint

[10] All samples in cross-section, consisting of the following: #1: paint fragment from a 17th century oil painting on copper; #2: copper substrate roughened with sandpaper & degreased with ethanol + a layer of pure cold-pressed linseed oil (code: Aa1); #3: same as the previous sample, but instead layer of lead white in cold-pressed linseed oil (code: Aa9); #4: copper substrate roughened with sandpaper, degreased with ethanol & rubbed with garlic + a layer of 20% colophony resin by weight in cold-pressed linseed oil (code: Ca5); #5: same as the previous sample, but instead layer of lead white in cold-pressed linseed oil (Ca9).

[11] All samples in cross-section, consisting of the following: #1: paint fragment from a 18th century oil painting on copper; #2: copper substrate + a layer of pure linseed oil (sample from D. Evenrigham's MA dissertation [17]); #3: copper substrate + a layer of lead white in linseed oil (sample from D. Evenrigham's MA dissertation [17]); #4: copper substrate roughened with sandpaper, degreased with ethanol & rubbed with garlic + a layer of 20% drying oil mixed with cold-pressed linseed oil (sample from N. Broers' MA dissertation [16]; code: Ca3); #5: sample Ca9 from N. Broers' MA dissertation [16] (see composition above). Samples #2 & #3 were artificially aged *; samples #4 & #5 were naturally aged. * Ageing conditions not available.

layer, though with lower concentration. The latter is reported as being '…either impurities of the metal or its migration through paint…' [19, p. 79].

For this research, μ-PIXE analysis consisted of the acquisition of 2D elemental distribution maps of four original paint cross-sections (S1–S4) from *Visitation* (see Appendix IV.1 for instrument description and experimental conditions). The presence of copper was verified in all the samples upon the acquisition of elemental maps, not only in areas corresponding to copper-based or copper-containing pigments, but also in areas corresponding to the preparatory layer, more or less evident depending on the sample (see Appendix IV.5, Fig. IV.8-IV.11). The ground layer in all the samples had been previously characterized by μ-Raman as not having a single copper pigment in its composition (see Table IV.3 in Appendix IV.4). Therefore, the presence of copper may be interpreted as a sign of migration from the support; and/or can be related to the presence of the copper carboxylate layer that has been shown in OM of cross-sections to "stain" the ground layer in some areas. To confirm the results of the elemental maps obtained for the cross-sections (S1-S4), raster areas in the ground layer were chosen, originating X-ray spectra which are shown in Fig. IV.12-IV.15 of Appendix IV.5. Copper was detected in the ground of all the samples, with a higher or lower concentration, as can be deduced from the intensity of the peaks in each PIXE spectra. The sample which showed the highest amount of copper is S2, and the one with the lowest is S3 (see Appendix IV.5).

PART 2

4. Scientific investigation: testing 4 consolidants for oil paintings on copper supports

4.1. Objectives

The main reason for having carried out this investigation is the obvious poor condition of *Visitation* in terms of adhesion of the paint composite to the copper support (see Section 2 – Condition Report). Since published information concerning the consolidation of oil paintings on copper is rather scarce, an original experimental design was created and put into practice with the final aim of understanding which of the studied substances – Paraloid B-72; Paraloid B-67; Paraloid B-44; Mowilith 20; Beva 371b; Laropal A81; and Regalrez 1094 – would be the most suitable to use as a consolidant during treatment of the painting (see Appendix V.2, Table V.3 for characterization of the polymers based on the literature).

In an attempt to approximate the results of the experiment to what might actually happen while consolidating the painting, a series of copper coupons was produced to work as substrates. The coupons came into contact with the consolidants either by receiving a coating, or by having oil paint fragments adhered directly to their surfaces (see 4.4). The samples went through accelerated ageing cycles, to understand how the materials would behave in the long term.

Therefore, it is the main purpose of this investigation to understand how these three types of materials – metal (copper); synthetic polymers (consolidants); and paint (oil paint) – are interacting with each other. This can be visualized by dividing the interactions in two types which are active at different sites in the stratigraphy: the interaction between the polymers and the copper substrate; and the interaction of the polymers in relation to both paint and copper. For this work, research was primarily focused on the study of the polymers and copper substrates.

At a visible level, the polymeric films' performance in terms of adherence to the copper substrate was to be assessed: would they continue to be well adhered after ageing, or would they detach? In terms of detachment, would this be complete or partial (e.g. the formation of blisters)? Would there be any visual evidence of copper corrosion at the site of the polymer coatings?

At a chemical level, the aim was not only to evaluate possible reactions of the polymeric films with the copper, such as corrosion products, but also to discover if there would be evidence of the diffusion of copper ions from the substrate into the polymeric matrices (for reasons explained below in 4.5.1). If copper ion migration is occurring, the next questions were, to what degree and extent of penetration? What is the possible role of the copper ions in the degradation of the polymers under study? Are the diffusion processes different depending on the condition of the copper substrate (cleaned or oxidized), and on the type of polymer applied? And is the presence of copper ions in the polymer affecting its adherence to the substrate?

4.2. Literature review & considerations on the consolidation of oil paintings on copper

Isabel Horovitz, a paintings conservator with expertise in the study and treatment of paintings on copper, appears to be the only person thus far who has carried out a methodical experiment, though empirical, with the aim of evaluating different consolidants for paintings on copper. Her experiment

started in 1981, when 12 consolidants were applied to a sheet of copper and after ageing for 1 month, were '…judged visually…' ([1], p. 47). The results of natural ageing of these consolidants were then reported in her article of 1986: "Paintings on copper supports: techniques, deterioration, and conservation" [1].

After 14 years, in 1995, she continued her experiments with a focus on 8 different consolidants which were also empirically tested, but this time assessed after 1 month of being applied, according to three parameters: visible reactions with the copper substrate; level of adhesion to the copper; and handling properties during application. These results, including a re-evaluation of the ones applied in 1981, are summarized in her article from 1996: "The Consolidation of Paintings on Copper Supports" [24]. Table V.1 in Appendix V.1 presents a summary of the assessments reported for each tested consolidant at both times (1986 and 1996).

Horovitz consistently reported that Beva 371, Paraloid B-72, and Poly(vinyl acetate) solvent solutions (Mowilith 20 or AYAB) were the most suitable of the consolidants she studied.

For this thesis, a literature review of consolidants for paintings on copper was carried out. Few additional sources aside from Horovitz [1; 10; 24; 25] were found [26-28]. Besides the consolidants referred above in Table 1, only two different ones were reported: beeswax/resin mixtures, in [25] and [27]; and Paraloid B-44, in [10] and [25]. According to the sources consulted, Paraloid B-72 appeared the most often [1; 10; 24-26; 28].

Horovitz has pointed out a number of things that should be taken into consideration when choosing a consolidant specifically for paintings on copper, and about the process of consolidation *per se*, summarized here:

- The consolidant must be capable of adhering paint to metal efficiently [24];
- The consolidant must not react negatively with the pictorial layers, for example causing paint swelling [24] and with the copper support, for example originating the appearance of new corrosion products [2]. These are the reasons given for avoiding, for example, aqueous-based consolidants and beeswax/beeswax-containing materials [1; 10; 24; 25];
- The solvent used will only be able to evaporate through paint cracks or paint-loss areas due to the copper support being non-porous, and it will likely do so at a slow rate [10; 24; 25], which suggests that there could be prolonged contact with the paint composite. Such contact could result in damage, causing swelling of the ground/paint layers [24]. Horovitz warns '…it is important to consider the amount of solvent being introduced under a paint film, particularly in the case of a painting with large blind blisters or cleavage…' [24, p. 278], due to the possibility of such areas retaining higher amounts of solvent.
- The viscosity of the consolidant solution: if it is too thick, it may not penetrate effectively into the paint composite and fill in all the existing gaps, and as she notes, '…there is a danger that excessive bulk may be introduced, the removal of which may be difficult…' [24]. However, a more viscous solution may in fact prove useful when adhering isolated paint flakes to the support directly [24]. Alternatively, if it is too fluid, although it will enter the paint composite easily through cracks and edges of losses, a higher proportion of solvent-to-resin will be introduced, which may not deposit sufficient consolidant to results in effective adhesion [24];

- Due to the copper having high thermal conductivity, the use of heat (e.g. from a heat spatula when consolidating paint with Beva 371) must be very cautious. Horovitz states that it may cause negative effects on the painting, such as compromising an already fragile level of adhesion between the pictorial layers and the support, sometimes beyond the areas being treated [1; 10; 24].
- Due to the support being made of metal, any consolidant that needs to be applied warm (such as Beva 371) will cool rapidly when in contact with the copper, which will affect its viscosity and reduce its ability to flow into cracks and lacunae between the paint composite and the copper [10; 24]. In these cases, Horovitz notes that overall gentle heating (to 40ºC [24]) in the areas surrounding those being treated may prove helpful, in the sense that it keeps the consolidant in a fluid state, therefore aiding its penetration underneath the paint composite [1; 10]. She suggests that warm air pencils and silicone-tipped modelling tools are alternatives to heated spatulas [10; 24].

4.3. The selection of consolidants to study

For detailed information about each consolidant including relevant chemical & physical properties and reports on their ageing behaviour, see Appendix V.2, Table V.3.

Initial thoughts

When beginning to discuss and reflect upon the consolidants which were to be included in the experiment (having Isabel Horovitz' guidelines in mind), it was thought that the use of substances as simple as possible, i.e. composed of one ingredient only, would be preferred over mixtures or dispersions, since this would reduce the variables in evaluating their performance. The role of ingredients in complex commercially prepared mixtures (e.g. Beva 371) would be more difficult to evaluate, and dispersions are normally aqueous based and would therefore be eliminated at the start. In addition, knowing exactly what was applied at a chemical level may help to anticipate possible future reactions between the painting materials and the consolidant. Despite being a complex mixture, Beva 371b was included as noted below, because it was recommended in the literature.

Initial choices

The results of the experiments described in the literature were taken as the starting point in the selection process for the consolidants to be studied in this investigation. Since Paraloid B-72; Mowilith 20; and Beva 371 were reported to be the best options, they were automatically included.

Paraloid B-67 was included as a possible alternative to B-72 because it dissolves in White Spirit, a solvent less likely to be aggressive to the paint layers due to having a low aromatic content (as opposed to toluene or xylene, for example); and also because it has a higher glass transition temperature (T_g) than B-72, meaning that in theory it would be less sticky and less prone to attract particles such as dust and dirt once applied[12]. However, should its ageing characteristics (see

[12] Although rated a 'Class A' resin by Feller in terms of photochemical stability [29] (i.e. a material '…of "excellent" quality suitable for use in conservation practice…' with '…at least 100 years of satisfactory service…' [29, p. 6]), Paraloid B-67 has been reported to cross-link with age [29; 30], becoming increasingly insoluble in solvents that are safe to use on an object [29]. If used with the purpose of consolidating paint to a copper substrate, such a change in solubility should not be a problem, since it is not feasible to remove once it penetrates the paint system.

Appendix V.2, Table V.3) change its physical properties, leaving it, for example, brittle, then its effectiveness at the copper/paint composite interface would be undermined.

Paraloid B-44 was included due to its being the main solid component of Incralac, a product which was designed specifically for coating objects made of copper and copper-based alloys. Incralac itself was not chosen as an option since it is a mixture of ingredients containing, besides B-44, toluene, xylene and methyl ethyl ketone (MEK), and also an unidentified UV absorber and corrosion inhibitor Benzotriazole (BTA) [31].

Laropal A 81 and Regalrez 1094 were included at the suggestion of Dr. Carlyle, due to being low molecular resins and with the aim of testing a new use for them. Although commonly employed by conservators as varnishes, it was thought that, since they are dissolved in low aromatic solvents, and are composed of small-sized molecules, they could possibly penetrate the paint composite easily and provide enough and effective adhesion between the paint and metal.

Pilot-project

Once the consolidants were chosen, the next question was to decide on the concentrations to be tested. A pilot-project was carried out to test their ability to adhere oil paint fragments to copper at three different concentrations: one high, one medium, and one low (see Appendix V.1, Table V.2).

Two types of oil paints were used: for the high concentration tests, a blue paint from a drawdown belonging to the 'Can to Canvas' project; and for the medium and low concentration tests, a white paint from a drawdown belonging to the 'HART' Project (see sample descriptions Appendix V). The reason for having changed the paint being tested was due to having the analytical characterization of painting's ground by the time the medium and low concentration tests were performed. Thus, the white paint from the HART project was chosen due to having points in common with the painting's ground composition; a lead white pigment bound in a drying oil (see Section 3).

The procedure consisted of adhering the paint fragments (with approximate dimensions of 1x2 mm) using the respective consolidants to a cleaned and degreased copper plate with a fine brush; waiting one day to give the solvents enough time to evaporate (inside a fume hood) and allowing adhesion to take place. Adhesive strength between the paint fragments and the metal was assessed empirically by applying pressure to the side of the paint fragment with a fine-tipped wooden stick using approximately the same pressure to each paint/consolidant sample.

Depending on their performance, i.e. their ability or failure to execute their function at the different concentrations, decisions were made as to whether they would continue to be studied or were eliminated at this stage; and to establish which concentration of consolidant would be used in the final experiment.

Results (see Appendix V.1, Table V.2) demonstrated that Paraloid B-44 and Paraloid B-67 failed to maintain adhesion of the paint fragments to the copper at both medium and low concentrations, which led to their elimination. Regalrez 1094 was tested at only one concentration (high) and was eliminated since it was still in a semi-liquid state after 24 hours (and thereby was judged to be taking too long to dry, leaving the paint composite in prolonged contact with the solvent). As for the remaining consolidants, Beva 371b, Mowilith 20 and Paraloid B-72 performed well at the medium concentrations,

and Laropal A 81 at the lowest concentration. Therefore, these consolidants were chosen for further study at those concentrations.

4.4. Experimental design

A total of thirty six copper coupons (dimensions: 2.5 x 1.5 cm) were prepared from a single sheet of copper 0.07 cm thick (the same thickness as the painting's copper support). The copper sheet was reported to be prepared industrially from a very pure alloy (99% copper).

Each coupon in this experiment has a unique combination of features (see Table 1). More detail is available in Appendix V.3, Table V.4 and Fig. V.1, with the experimental procedure in Appendix V.4.

- Coupons were either cleaned (polished and degreased), or pre-oxidized in a controlled environment before the polymers were applied;
- Two identical sets of coupons were either aged naturally in ambient conditions (monitored lab environment) (Set 1), or artificially inside a climatic chamber (Set 2);
- Coupons were either left without coating (a) as controls, coated with a single layer of consolidant applied by dipping (b), or had oil paint fragments adhered directly to their surfaces with each consolidant (c);

Table 1 – Summary of the copper coupons used in the study

Coupon number	Condition of the surface	Ageing conditions	Description
1 + 2	All odd numbers: **cleaned** All even numbers: **pre-oxidized**	**Ambient (Set 1)** (in monitored lab environment)	**Set 1-a:** Coupons with bare metal/nothing applied
3 – 10			**Set 1-b:** Coupons coated with a single layer of consolidant by dipping
11 – 18			**Set 1-c:** Coupons with oil paint fragments adhered directly to the surface
19 + 20		**Artificial & accelerated (Set 2)** (in climatic chamber)	**Set 2-a:** Coupons with bare metal/nothing applied
21 – 28			**Set 2-b:** Coupons coated with a single layer of consolidant by dipping
29 – 36			**Set 3-c:** Coupons with oil paint fragments adhered directly to the surface

Preparation of the copper coupons: Clean vs. Oxidized surface

Coupons having an oxidized surface as a starting point were included to represent the surface of the painting's copper substrate, which is currently oxidized where exposed to air (e.g. in lacunae, see Section 2, Condition Report). Oxidation was achieved by placing freshly-cleaned coupons, polished and degreased (see Appendix V.4), in a closed container with a very humid and warm environment (T=60ºC) inside. After remaining in the controlled environment for 23 days, the coupons were coated with copper oxide layers free of any other copper corrosion products. The simple oxidation layers

meant that other variables from other corrosion products were not present at the outset of the experiment. A set of cleaned copper coupons were included for comparison with the oxidised set.

The polymeric coating ('b')

In Sets 1 & 2, pairs of oxidised and cleaned coupons (numbers 3-10; and numbers 21-28), received a single thin coating of a given consolidant. Consolidants were applied by dipping, thereby covering both front and back surfaces (see Appendix V.4). This was done not only with the purpose of studying diffusion processes of copper ions from the substrate into the polymeric matrices (a topic addressed below in 4.5.1.), but also because, when applied to the painting, the consolidant will be deposited at the interface between the ground layer and the copper support most likely in a thin film similar to those achieved on the copper coupons. This experimental procedure was adapted from the PROMET guidelines [32-34][13].

The oil paint fragments adhered with consolidants ('c')

In Sets 1 & 2 pairs of oxidized and cleaned coupons (numbers 11-18; and 29-36) received three oil paint fragments adhered directly to the copper surface using each of the consolidants under study (see Appendix V.4). This modelled a situation analogous to that of the treatment of the painting – in terms of having a stratigraphy made of a copper substrate with oil paint on top and the consolidant in between. The aim was to test the ability of each consolidant to adhere the paint to copper.

Ageing conditions: Unaged (Set 1) vs. Artificially Aged (Set 2)

Set 1 coupons (numbers 1-18) were left in ambient conditions, with a dust cover of polyester film (Melinex®) to age naturally as a comparison with Set 2 coupons (numbers 19-36), which were placed in a climatic chamber for artificially accelerated aging (see equipment in Appendix VI), where they were left for a total of 60 cycles of 24 hours (h), in two separate periods of 30 cycles each.

Using the PROMET guidelines as a base [32], the coupons in the climatic chamber were exposed to fluctuations of temperature (T) and relative humidity (RH) consisting of two periods within each cycle of 24h, one with "normal" conditions (lasting 8 hours), and other with "extreme" conditions (for 16 hours), as described in Table 5.

Table 2 – Artificial ageing conditions for 1 cycle of 24h recommended by PROMET [32]

Ageing cycle	Division of the cycle in two periods of time (t)		
1 cycle of 24h	Normal conditions	t = 8h	T = 23ºC RH = 55%
	Extreme conditions	t = 16h	T = 35ºC RH = 90%

[13] PROMET (standing for "PROtection of METals") is a European interdisciplinary research project active between 2004-2008, involving 21 partners from 11 different countries in the Mediterranean basin. It had two main objectives:

1) To develop new strategies to monitor the corrosion of metal objects in museums using portable analytical techniques (LIBS; μ-XRF);

2) To develop and test new materials for the protection of metals collections (coatings and corrosion inhibitors). For more information, see < http://cordis.europa.eu/result/rcn/51904_en.html> or [34].

4.5. Experiment results

4.5.1. The diffusion of copper ions into the polymeric matrices

Research was directed to the study of the diffusion of copper ions into the matrices of the polymers under study since, according to the literature, the presence of metal particles inside polymeric systems, either in the form of individual atoms or clusters, or as metallic compounds, has been seen to contribute to their degradation [36-39]. This is due to the metals acting as catalysts in degradation processes such as thermal-oxidative degradation and auto-oxidation [36-39], which can result, among other effects, in poor physical properties [39], loss of material [36], or undesirable colour development [39].

However, the role that metals or metallic compounds may have is rather complex, and is influenced by interconnected factors, such as: the nature of the polymer in contact with the metal (its Tg, degree of crystallinity, molecular weight, etc.) [41]; the type of metal (its valency, oxidation state, etc.) [39]; and the environmental conditions to which the polymer/metal composites are exposed [37]. This implies that general assumptions must be treated with caution, since the diffusion behaviour happening in a given metal-polymer composite is very much dependent on the individual chemical interactions deriving from that combination [36; 40].

It is important to note that the literature survey undertaken reveals an absence of published studies focusing specifically on the diffusion of copper ions into the matrices of Paraloid B-72, Mowilith 20, Laropal A 81, and Beva 371b coatings. Articles addressing the phenomenon of the diffusion of copper (and even other metals) into polymeric materials were found, but all in other areas of Science such as microelectronics, nanomaterials and biomedical engineering. Usually the processes studied have as their starting points either the deposition of very thin metallic layers on top or on both sides of polymer substrates, or the intentional addition of metal particles to the polymers. Only one author, Hansen [18], was found to consider the role of migration from a metal substrate (copper) into the polymer coating, in that case, by casting polymeric films of a corrosion inhibitor (poly-N-vinylimidazole – PVI) on top of copper coupons. Thus, the theory and hypothesis presented here are based on literature which deals with different case-studies. However, since this phenomenon is proved to happen based on the literature, the theory behind it may be extrapolated to the results found with this experiment.

Hansen [35] has presented two plausible mechanisms for the diffusion of copper species through polymer films which are applied on top of copper coupons (reproduced in Figure 4) after detecting their presence in depth by XPS (X-ray Photoelectron Spectroscopy). The situation he describes may be similar to what could happen in the coupons of this experiment.

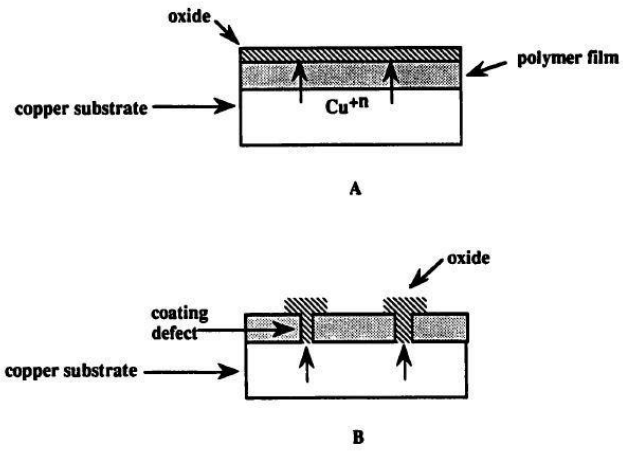


Figure 4 – Schematic of possible copper migration mechanisms: A) matrix-assisted diffusion; B) defect diffusion (Source: Hansen, 1994, p. 133)

The first diffusion mechanism is termed “matrix-assisted diffusion”, and involves the migration of copper ions through the polymeric film [35; 36; 38]. The second mechanism is termed “defect diffusion”, and involves the migration of copper mainly through defect areas in the film (e.g. pinholes and regions where it is very thin) up to the surface, where it is deposited and becomes oxidized [35].

Copper, being a noble metal (along with Au, Ag, and Pd), has been classified as being a low-reactivity metal, meaning that it interacts weakly with polymers at a physical and chemical level, although it is able to diffuse prominently in some, especially if the temperatures which surround the polymer/copper composite are higher than the polymers’ Tg [40; 41]. In this experiment, polymers were exposed to a maximum temperature of 35ºC while ageing inside the climatic chamber. This is very close to both Mowilith 20 and B-72 Tg’s of 36ºC and 40ºC respectively (see Appendix V.2, Table V.3).

4.5.2. Techniques for studying the diffusion of Cu ions into polymers

After an extensive investigation of the analytical techniques suitable and commonly used to study metal ion migration into polymers, Rutherford Backscattering Spectroscopy (RBS) was chosen for this work. RBS, described as “…ideal for investigations of diffusion near surfaces…” and having a good “…sensitivity to heavy elements…” is “…an excellent method for depth profiling of heavy elements in polymers that are usually made up of H, C, O and N...” [42, p. 446], as are the polymers under study. Another strong reason for this choice was the fact that the polymers can be studied in situ without being separated from the copper coupons.

However, unless complemented with results from other techniques (such as electron microscopy), the interpretation of RBS results should be made with caution since metal diffusion into the polymers can be misinterpreted due to the possibility of the presence of metal clusters at the polymer/metal interface, and not located throughout the thickness of the polymer film [43]. As explained below in 4.5.4.1, another problem that can affect the evaluation of RBS results is beam damage of the polymeric films, even when the beam is used with a very low current (less than 1nA).

Scanning Electron Microscopy (SEM) technique together with elemental mappings was selected to complement the information given by RBS, to check if copper was detected in the films specifically.

4.5.3. Visual monitoring of the polymers

The appearance of all the coupons was observed and captured digitally both overall and in detail.

With the aim of ensuring the exact lighting conditions when recording the coupons before, during, and after ageing, and to achieve good image quality, the images were taken with a flatbed scanner (see equipment in Appendix VI) at a very high resolution (3600 dpi). This method was adapted from one described in a PROMET-based article by Wolfram, Brüggerhoff and Eggert [32], where coupons were also scanned using similar conditions (1200 dpi).The resulting images were very satisfactory, except for a minor problem: shiny metal surfaces such as those presented by the clean coupons, reflect light from the scanner while the images were being acquired, resulting in images where these surfaces appear darkened. See images of scanned coupons in the supplied DVD.

No visible products derived from reactions between the polymers and the coupons were observed, suggesting that these polymers are initially chemically compatible with the copper substrate.

4.5.4. Analysis and discussion of results

4.5.4.1. RBS

RBS analyses were performed on the artificially aged coupons with a polymeric coating (Set 2-b: coupons 21-28, aged for 60 days). For details on the RBS instrument and experimental conditions, see Appendix V.4.

Table 3 shows the thicknesses for each film and the copper content for each coupon after fitting the experimental data. For individual interpretation of each result, see Appendix V.5.

Table 3 – Thickness and copper content detected in polymeric films analysed with RBS

Coupon no. & type of coating		Thickness (x10^{15} at/cm^2)	Copper content (at. %)
21	Paraloid B-72 on clean coupon	6500	0.17
22	Paraloid B-72 on oxidized coupon	not recorded	not recorded
23	Mowilith 20 on clean coupon	6200	0.10
24	Mowilith 20 on oxidized coupon	1200-7400	0.03-0.10
25	Laropal A81 on clean coupon	< 20	not recorded
26	Laropal A81 on oxidized coupon	< 20	not recorded
27	Beva 371b on clean coupon	17500-19500	0.05
28	Beva 371b on oxidized coupon	not recorded	0.05

The Laropal A 81 films are extremely thin (less than 20x10^{15} at./cm^2, roughly equivalent to less than 3 nm), so no realistic information can be extracted about the Cu diffusion.

The absence of data for coupons 22 and 28 is most likely related with the beam damage produced during the measurements (further explained in Appendix V.6 in individual interpretation of each spectrum).

Based on the data obtained, Mowilith 20 produced the thinnest coatings (besides Laropal A 81); and Beva 371b the thickest. In some cases (coupons 24 and 27), RBS also detected thickness variations within the same film, indicating that the application of the coatings by dipping and consequent horizontal drying did not produce perfectly even coatings.

Regarding copper diffusion, the results appeared to show that Paraloid B-72 (B-72) received the highest amount of diffused atoms, and Beva 371b the lowest. However, in order to verify these results, visual evidence of the analysed areas after measurement is essential, therefore OM photographs were taken. They demonstrated that apparently all consolidant films suffered damage from the RBS beam during analysis, resulting in darkened areas or in the creation of localized bubbles in the film (see examples in Appendix V.6).

Consequently, the RBS results may be misleading and are inconclusive, since it is not possible to discriminate between diffusion corresponding to processes that occurred before RBS analysis (deriving from an interaction between the two materials); or those processes resulting from beam

damage. Visual evidence suggests the latter situation: that during analysis (approximately 30 min each) the beam progressively erodes the film, reducing its thickness and thus shifting the Cu signal towards higher channels, indicating the presence of Cu at the surface; or possibly copper appearing as a result of changes in the film caused by the beam.

One interesting result of RBS is that films applied on the oxidized coupons (numbers 22, 22, 26 and 28) appear to result in spectra with poorly defined film thickness areas, whereas the opposite is found for films applied on clean coupons (21, 23, 25 and 27). This suggests that the presence of a metal oxide layer plays a role in the RBS's ability to acquire well defined spectra, probably due to the fact that such a layer has a particular nano-texture, and in cleaned copper surfaces such a layer is not as evident (when dealing with very thin layers, RBS is extremely sensitive to surface roughness).

4.5.4.2. SEM/EDS

To help understand the RBS results, SEM analyses were done to detect the presence of copper in samples from the artificially aged polymeric films (Set 2-b). Two polymer films were analysed with this technique as these were the most likely to be chosen for consolidation: B-72 (from coupons 21 and 22); and Mowilith 20 (from coupons 23 and 24)[14]. Five micro-samples from each coupon were collected using a number 11 scalpel blade, and were adhered to carbon tape with the surface in contact with the copper facing up (to detect copper more easily should it be there). For SEM/EDS instrument and experimental conditions, see Appendix V.5.

Elemental mapping did not detect any copper in any of the films. In the spectra collected, only peaks of C and O appeared, related to the chemical composition of the polymer films. The absence of copper suggests that no diffusion processes had occurred, either because these polymers and the copper do not interact in that way, or because the samples were not left to age long enough for such processes to occur.

However, interesting data was collected regarding the morphology of the films: the samples showed consistent visual differences in the polymer films depending on the type of surface they had coated, i.e., clean vs. oxidized copper. Films applied on clean, polished copper surfaces appeared to be more uniform; whereas films applied on oxidized surfaces exhibit irregularities and cavities of variable dimension (see Figs. V.11-V.14 in Appendix V.7).

B-72 produced the most homogeneous films, especially when applied on a clean copper surface. Mowilith 20, on the other hand, does not appear to be as homogeneous (compare Figs. V.11 & V.12 with V.15 & V.16) due to exhibiting multiple dark rounded shapes surrounded by whiter areas that were actually created during analysis, as a result from beam damage.

[14] Laropal A81 had been eliminated at this stage as explained in 4.5.5; and Beva 371b was not analysed due to the appearance of green spots in a coating of it on one naturally aged coupon (# 9). Initially thought to be products derived from a reaction between the copper substrate and a component of Beva 371b, it was later concluded that the green spots may simply indicate that the Beva 371b film was not a very effective protective coating against corrosion.

4.5.5. Conclusions

The answer to the main question in this investigation, whether copper diffuses from the substrate into the polymers under study remains inconclusive, primarily due to the analytical results. RBS results were very inconclusive due to the polymeric films being very sensible to beam damage, demonstrating that this technique does not seems the most suitable for this study. SEM/EDS results from the analytical design used (topographical orientation) indicate that copper diffusion did not occur, since copper was not detected within any of the polymeric films sampled.

The presence or absence of a copper oxide layer underneath the films appears to yield differences in the polymer film morphology, probably due to the fact that an oxidized layer is more textured than a smoothed surface, therefore producing an analogous texture in the films which is particularly evident on the side in contact with the copper substrate. These findings have shed some light on the potential morphology that the chosen consolidant layers will acquire once applied to the painting, since the surface of the copper plate is oxidized. They might also explain why RBS measurements seemed to be affected by the presence of oxidized layers, since the films in these cases have been shown to be nonhomogeneous.

During sample collection of the artificially aged materials, it was possible to understand by touch the level of internal cohesion of the polymers and to evaluate their adhesion to the copper. B-72 produced cohesive films, well adhered to both clean and oxidized copper substrates; Mowiltih 20 also yielded cohesive films, but exhibited a lower level of adhesion in comparison with B-72 films. The Mowilith 20 separated from the copper in a manner suggesting that there was air between the copper and the film (as in a blister). This was especially evident on the oxidized coupon. Films of Laropal A81 were extremely brittle and easily detached from the support on both clean and oxidized coupons. For this reason, Laropal A81 was excluded as an option. Films of Beva 371b remained soft and were well adhered to both clean and oxidized coupons.

SEM/EDS images showed that both B-72 and Mowilith appear to form homogeneous films, although altered due to beam damage. B-72 was considered preferable, as the simpler of the two polymer systems. While Beva 371b appeared unchanged throughout ageing, the complex mixture of materials in its formulation suggests that further study of its individual components would be needed before it could be used for consolidating loose oil paint on copper substrates. As noted in the introduction, concern has been expressed that the plasticisers present in the formulation could migrate into the paint composite.

Despite the lack of evidence of copper diffusion into the polymer films studied, the PIXE results (detailed in Section3 and Appendix IV.5), which confirm copper diffusion from the substrate into the ground layer from *Visitation*, indicate that the copper plate can be far from inert in relation to layers applied to its surface. In that case it is likely that the interaction between the ground and copper plate is related to the presence of oil, either as a separate layer or as the binder in the paint/ground composite, but this interaction does indicate that concern regarding the activity of the copper in relation to contact with new layers is warranted.

4.6. Further work

The SEM/EDS analysis could be repeated with the polymer films mounted as cross-sections to confirm (or refute) the results obtained with the topographical sample orientation. To protect the films from dissolution in the embedding resin, they would have to be pre-coated with Parlylene® prior to embedding [44].

In order to gain a better understanding of the different film morphologies in the presence of clean vs. oxidized copper, SEM/EDS analysis of each type of copper surface alone (without films applied) could be useful, for it could provide interesting evidence on their nano-topographies.

The part of the experiment with adhered paint fragments (Sets 1-b & 2-b) should be further investigated to understand if copper diffusion into the paint can be detected, since in this case the oil binder had fully dried. These results would be compared to results from the PIXE analysis of the original paint samples from the painting, which showed copper diffusion from the painting support into the ground layer in all the samples analysed. Since it is unclear whether the diffusion occurs while the paint is still wet, or is a function of ageing over time, this investigation of dried paint could be informative.

A study even closer to what is happening in these systems would be to apply paint covering a copper support completely, and then perform accelerated ageing so that the two layers would have time to interact and form the interfacial layers which are normally formed and observed in these paintings. The consolidants could then be introduced and aged within this already aged paint stratigraphy, and their behaviour in relation to both the copper support and the interfacial products could be studied afterwards.

Other analytical techniques for future research on copper diffusion into polymers that may not damage the films during analysis have been identified in the literature [45]: FIB-SEM (Focused Ion Beam-Scanning Electron Microscopy); XPS (X-ray Photoelectron Spectroscopy); and TEM (Transmission Electron Microscopy). These would be well worth investigating.

5. Summary and conclusions

It was possible to place the execution of *Visitation* to between the 16th and 18th centuries by combining the visual information based on the style of representation (thought to be Flemish, from around the 16th/17th century); the analysis of the costumes of two characters (belonging to the second half of the 16th century); and materials characterization through analytical methods, which revealed the presence of the pigment lead-tin-antimony yellow which fell out of use by the mid to late 18th century.

Technical investigation of the painting's materials through the use of different analytical methods (OM; μ-FTIR; and SEM/EDS) allowed the characterization of three substances found at the interface between the copper support and the preparation layer, which are thought to be formed as a result from interactions between the two. These layers may or may not be responsible for the degradation of the painting in terms of paint flaking, and for this reason they should be further investigated in order to gain a better understanding of their role. The white-grey layer covering the copper support was found by μ-FTIR to have a quite complex composition with different carboxylated material that needs further investigation. The green layer commonly reported to exist in this kind of artwork was characterized also using μ-FTIR as being a copper carboxylate (copper oleate or linoleate), thus confirming what the literature describes; further investigation with SEM/EDS mapping on the underside of two paint fragments where this layer was present showed, as expected, a strong presence of copper in the corresponding areas. A transparent layer found on the underside of some paint fragments that appears to be a continuation of the green copper carboxylate was analysed with SEM/EDS; and copper was identified, thus suggesting that this layer might be the same substance as the copper carboxylate, only in a different state of formation. However, only molecular analysis of this layer (employing, for example, μ-FTIR) could confirm if both materials are in fact the same.

The interaction of the copper support with the paint composite was also investigated using μ-PIXE to detect the presence of migrated copper from the support into the upper layers. Analysis of four cross-sections revealed that this element exists in the ground layer in all four, to a greater or lesser extent, thus demonstrating that the materials in these preparation layers do interact with each other. Further investigations into the effect of copper inside these layers with the aim of understanding if it is contributing to their degradation should be done.

The investigation project which studied four different synthetic polymers to act as potential consolidants for the treatment of the painting, focusing specifically on copper diffusion from the substrate into the polymeric matrices, had no results due the RBS alpha particle beam damaging the polymer films during analysis. Supplementing analysis using SEM/EDS did not detect copper in samples of the same films, either indicating that these polymers and copper do not interact like that; or that the accelerated ageing cycles put into practice were not long enough for these processes to occur.

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Appendices

A digital Appendix (DVD) is supplied in order to provide all the images presented next with better resolution.

Appendix I – Overall Before Treatment photographs of Visitation

Figure I.1 – Normal light, front.

Figure I.2 – Normal light, back

Figure I.3 – Raking light from the right side.

Figure I.4 – Raking light from the bottom side.

Figure I.5 – Ultraviolet (UV) light, front.

Figure I.6 – Infrared (IR) light, front.

Appendix II – Before Treatment detail photographs of Visitation

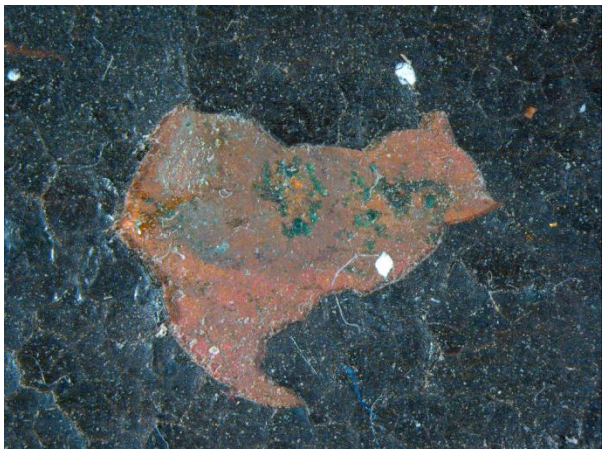


Figure II.1- Cu corrosion on paint loss (x16).

Figure II.2- White-grey layer with powdery substance (x50).

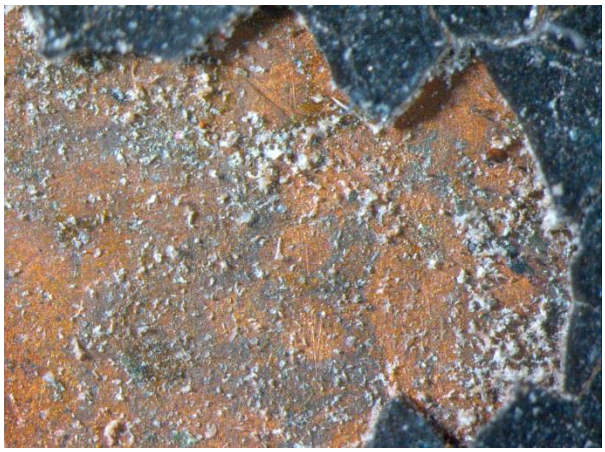


Figure II.3 – White-grey layer with powdery substance (x50).

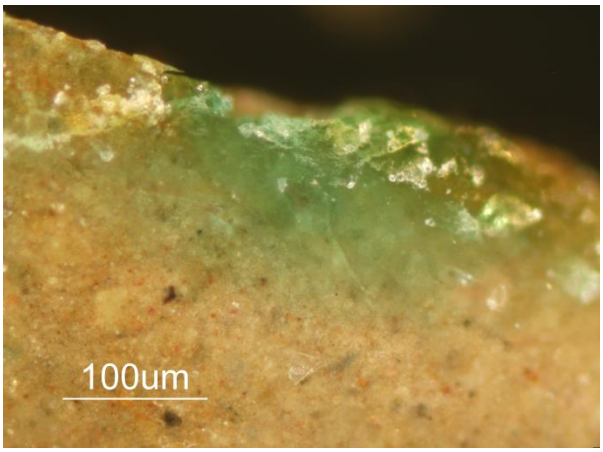


Figure II.4 – Green interfacial layer (x200).

Figure II.5 – Underside of paint fragment in normal light (left) and Filter set 5 (BP 395-440, FT 460, LP 470) for fluorescence (right) (x50).

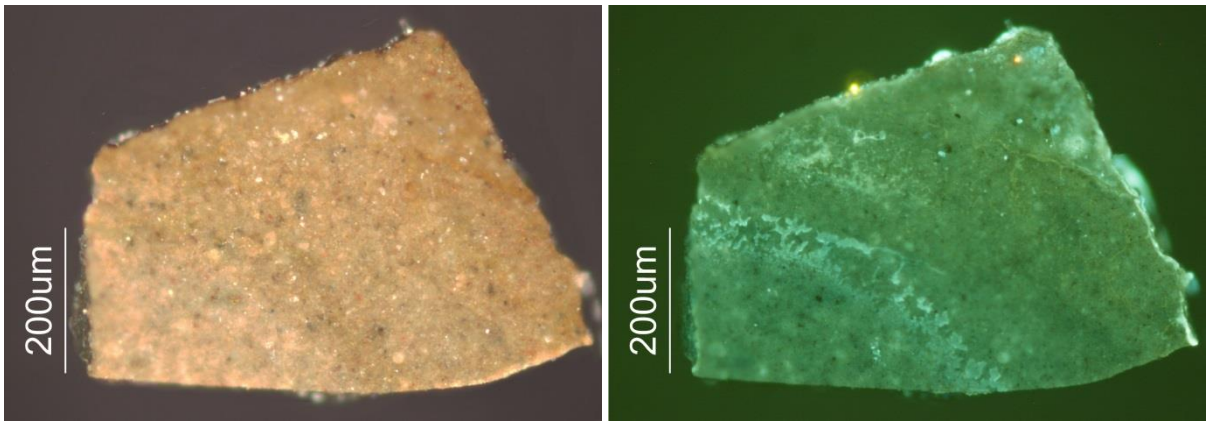


Figure II.6 – Underside of paint fragment in normal light (left) and Filter set 5 (BP 395-440, FT 460, LP 470) for fluorescence (right) (x100).

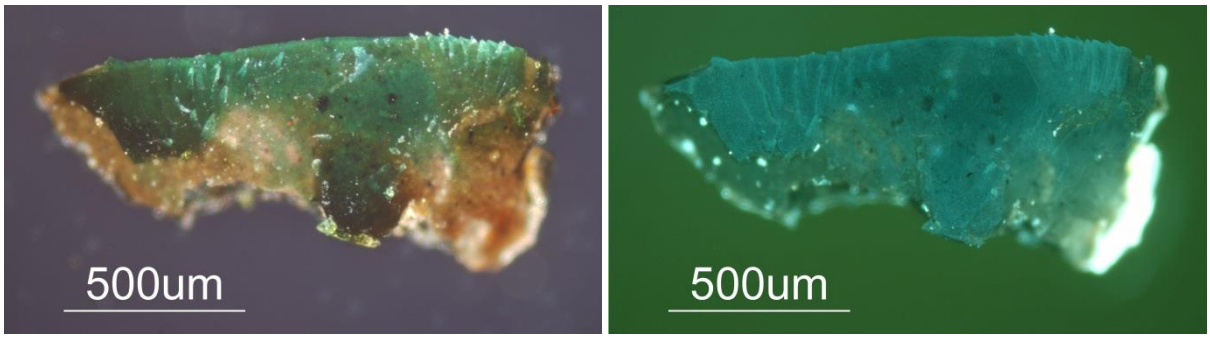


Figure II.7 – Underside of paint fragment in normal light (left) and Filter set 5 (BP 395-440, FT 460, LP 470) for fluorescence (right) (x50).

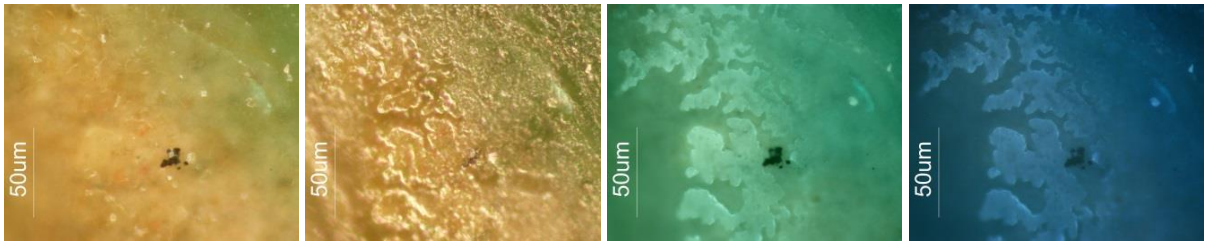


Figure II.8 – Detail of the underside of the paint fragment represented in Figure II.5. Left to right: normal light, bright field, Filter set 5 (BP 395-440, FT 460, LP 470) for fluorescence and UV light (x500).

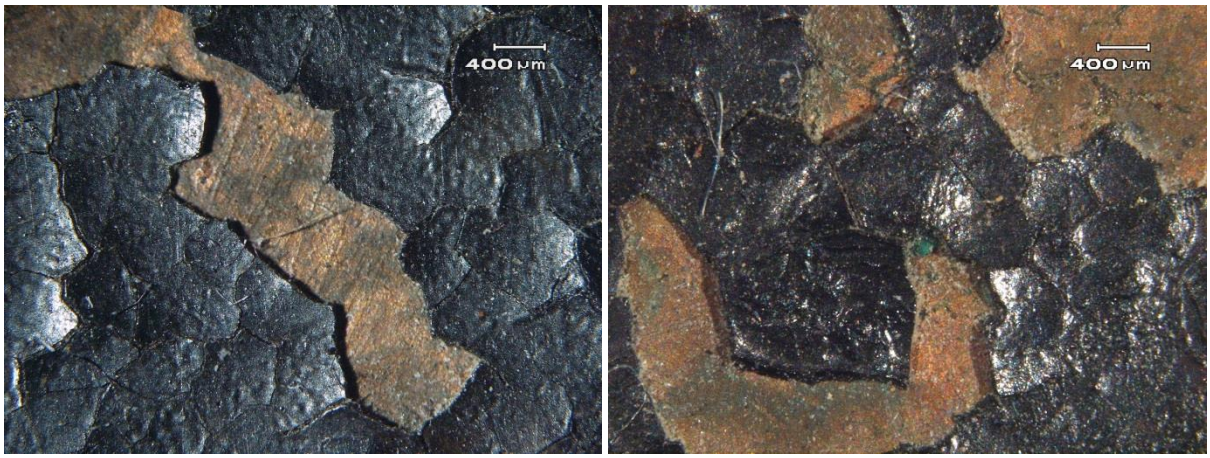


Figure II.9 – Two details of flaking paint (x40).

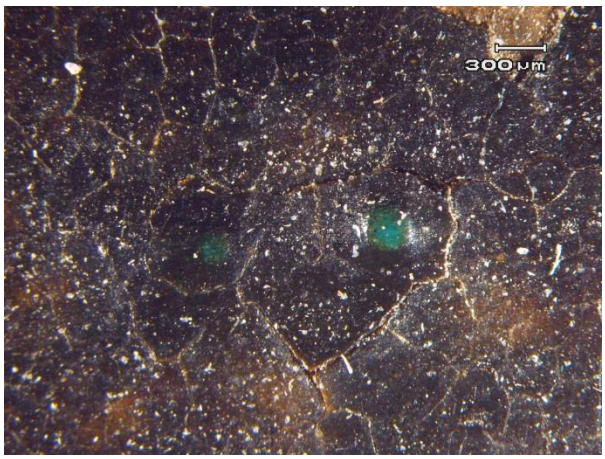


Figure II.10 – Green protrusions (x50).

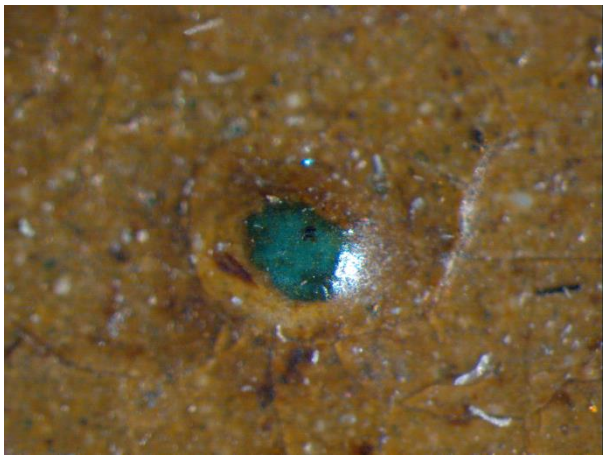


Figure II.11 – Green protrusion (x80).

Appendix III – Map of damages

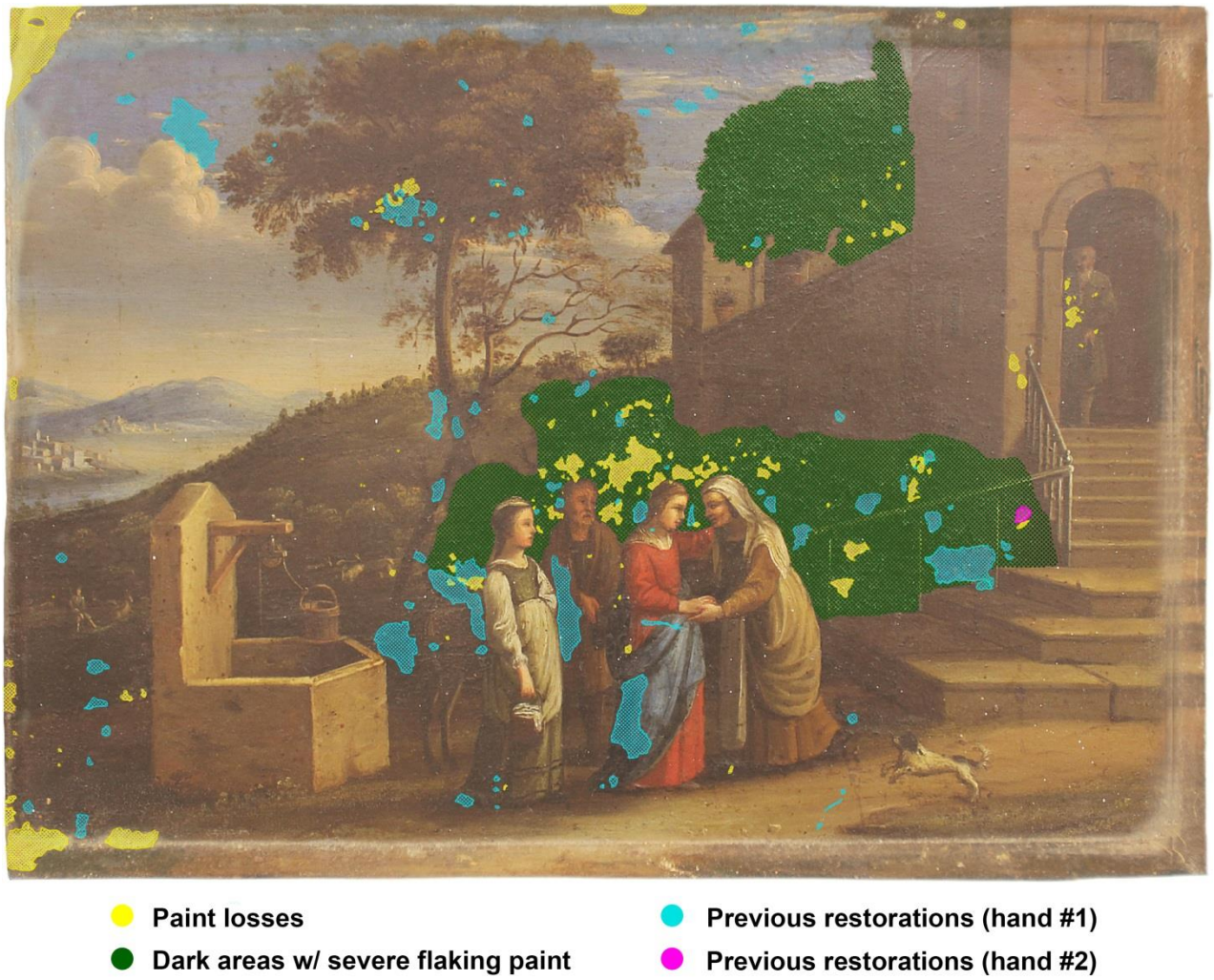


Figure III.1 – Mapping of *Visitation* condition.

Appendix IV – Materials analysis

Table IV.1 – Analytical strategy employed to study the painting's materials

Analytical technique	Purposes
μ-EDXRF	• Elemental qualitative analysis of the copper plate's alloy; • Overall elemental qualitative analysis of the pictorial layers.
μ-FTIR	• Molecular characterization of the paint binder; • Molecular characterization of the varnish; • Molecular characterization of the green interfacial layer formed between the support and the ground; • Molecular characterization of the whitish translucent interfacial layer covering the support.
μ-Raman	• Molecular characterization of pigments present both in the paint layers and ground.

Analytical technique	Purposes
μ-PIXE	• Elemental mapping and analysis of selected cross-sections to investigate copper diffusion from the support into the pictorial layers.
SEM/EDS	• Elemental mapping to investigate transparent layer found on the underside of some paint fragments (see Section 2).

Appendix IV.1 – Instruments description

All the analytical instruments used belong to FCT-DCR, with the exceptions of SEM/EDS, belonging to CICECO (Aveiro Institute of Materials), University of Aveiro; and Van de Graaff accelerator (used for μ-PIXE and RBS experiments) is located at Campus Tecnológico e Nuclear-Instituto Superior Técnico (CTN/IST).

➢ Photographic documentation

Studio photographs with normal and Ultraviolet (UV) light were taken with a Nikon D200 digital SLR (Single Lens Reflex) camera (with a 18-200mm f3.5-5.6G IF-ED AF-S DX VR Zoom-Nikon lens, zoom up to 11.1x; resolution 10.2 Mega-pixels). Photographs with Infrared (IR) light were taken with a Sony digital camera (DSC-F828, Cyber-shot, Zeiss, Super HAD CCD, 4colour. optical zoom up to 7x; resolution 8.0 Mega-pixels) equipped with an IR filter (Hoya, 58mm Infrared R72).

Detail photographs were taken with a Leica MZ16 stereomicroscope with a 7.1x to 115x zoom range lens, equipped with an integrated Leica ICD digital camera and a Leica KL 1500 LCD external cold light source with two flexible optic fibre cables.

➢ Optical Microscopy (OM)

The optical microscope is an Axioplan 2ie Zeiss microscope equipped with a transmitted and incident halogen light illuminator (tungsten light source, HAL 100); UV light (mercury light source, HBO 100 illuminator); and a digital Nikon camera DXM1200F, with Nikon ACT-1 application program software, for microphotographs. Samples were analysed with 10x ocular lenses and 5x/10x/20x/50x objective Epiplan lenses (giving total optical magnification of 50x, 100x, 200x, and 500x).
For the incident light (normal light) the samples were analysed under crossed polars – polariser and analyser filters; and for UV light the Zeiss filter set 2 [BP300-400, FT 395, LP 420] was used. The scales for all objectives were calibrated within the Nikon ACT-1 software.

➢ Micro-Energy Dispersive X-ray Fluorescence (μ-EDXRF)

X-rayfluorescence spectra were obtained using an ArtTAX spectrometer from Intax GmbH. Operating with a molybdenum (Mo) X-ray tube, focusing polycapillary lens and silicon drift electro-thermally cooled detector and a xFlash (Si drift) detector, with 170 eV resolution. The accurate positioning system and polycapillary optics enable a small area of primary radiation (ø ~70 μm) at the sample. Elemental compositions were obtained from the average of three independent spots, analysed with a tube voltage of 40KV and a current intensity of 600μA and live time 100s.

- **Micro-Raman (μ-Raman)**

Micro-Raman microscopy was done using a Labram 300 Jobin Yvon spectrometer, equipped with a He-Ne laser of 17 mW power operating at 632.8 nm and an external laser of 50mW power operating at 532 nm. Spectra were recorded as an extended scan. The laser beam was focused with a 506 Olympus objective lens (50x). The laser power at the surface of the samples was varied with the aid of a set of neutral density filters (optical densities 0.3, 0.6, 1). The spectra are shown as acquired, without corrections or any further manipulations.

- **Micro-Fourier Transform Infrared Spectroscopy (μ-FTIR)**

Infrared spectra were acquired using a Nicolet Nexus spectrophotometer coupled to a Continumm microscope (15xobjective) with a MCT-A detector cooled by liquid nitrogen. The spectra were collected in transmission mode, between 4000 – 650 cm-1, resolution setting 4 cm-1 and 128 scans, using a Thermo diamond anvil compression cell. The spectra are shown as acquired, without corrections or any further manipulations, except for the removal of the CO_2 absorption at ca. 2300-2400 cm^{-1}.

- **Electron Scanning Microscopy with Energy Dispersive X-ray Spectroscopy (SEM/EDS)**

A HR-FESEM Hitachi SU-70 Ultra-High Resolution Analytical Scanning Electron Microscope was used with a SE (secondary electron) detector coupled with a Peltier cooled B-U Bruker QUANTAX 400 EDS spectrometer. Samples were covered with a layer of carbon. The elemental maps were acquired with a voltage of 15.0kV (high voltage).

- **Particle Induced X-ray Emission (PIXE)**

Analyses were performed using the Oxford Microbeams® type nuclear microprobe with a lateral resolution of 3 μm available at CNT. Under vacuum conditions, a 2 MeV proton beam was used, with the current kept at 0.8nnA. Measurements were performed at normal incidence and the induced X-ray were detected with a Si Bruker SDD X-ray detector with an active area of $30mm^2$, and placed at an angle of 45 º to the beam direction. The OMDAQ V5.2 software was used for data acquisition and treatment.

Appendix IV.2 – Sampling areas for cross-sections (S), µ-FTIR (F) and µ-EDXRF points (●)

Figure IV.1 – Sampling areas for cross-sections (S), µ-FTIR (F), and µ-EDXRF (●).

Table IV.2 – Code for identification of cross-sections (left) and µ-FTIR samples (right)

Sample	Colour/Area
S1	Green (vegetation)
S2	Light blue (sky)
S3	Green & yellow (maid's dress)
S4	Dark green (tree)
S5	Black (vegetation)
S6	Light blue (sky)

Sample	Material
F1	Blue paint (sky)
F2	Varnish
F3	Green interfacial layer
F4	White-grey layer covering Cu support

Appendix IV.3 – Observation of cross-sections under OM with normal and UV light

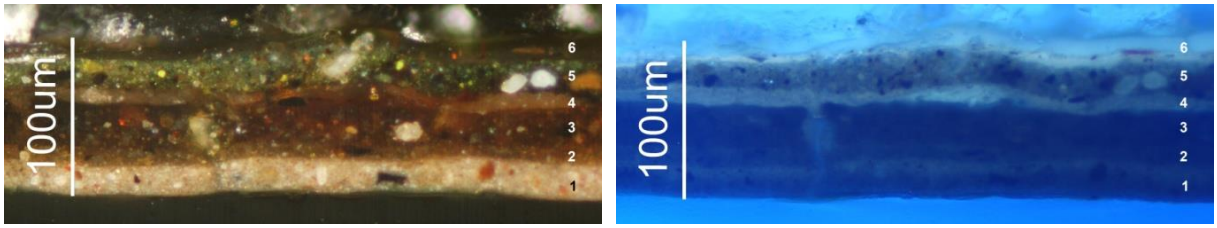


Figure IV.2 – Cross-section S1, photographed in OM with normal (left) and UV light (right), with layers numbered (x200). Layer 5 is considered to be overpaint since it is sandwiched between two layers of varnish, 4 and 6.

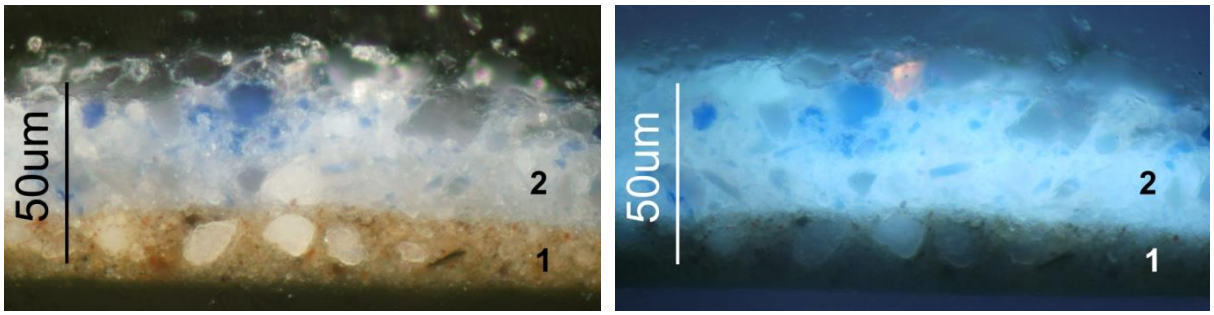


Figure IV.3 – Cross-section S2 (original), photographed with normal (left) and UV light (right), with layers numbered (x500).

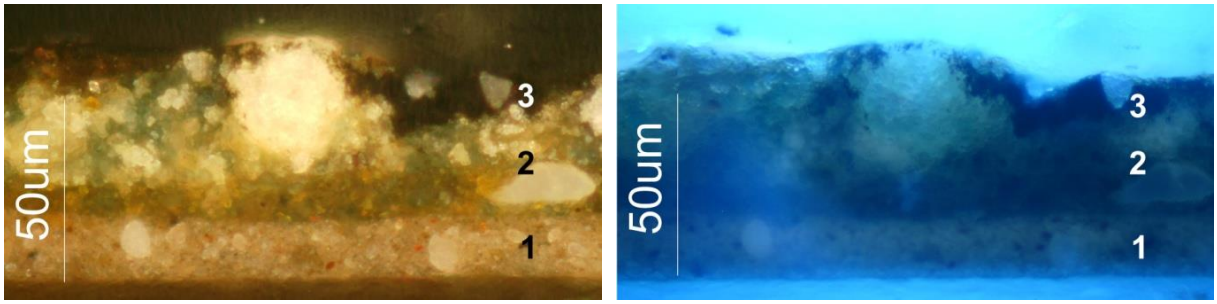


Figure IV.4 – Cross-section S3 (original), photographed in OM with normal (left) and UV light (right), with layers numbered (x500).

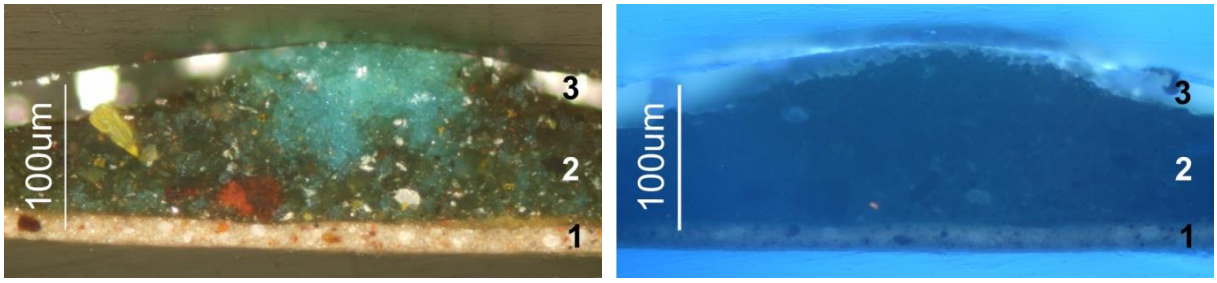


Figure IV.5 – Cross-section S4 (original), photographed in OM with normal (left) and UV light (right), with layers numbered (x200).

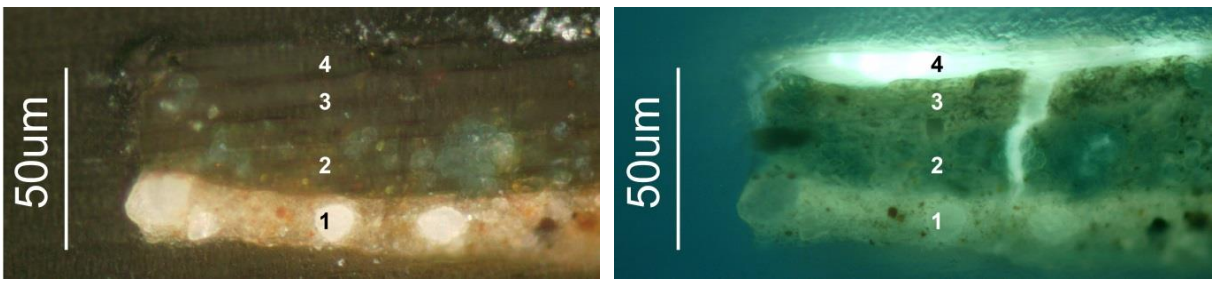


Figure IV.6 – Cross-section S5 (original), photographed in OM with normal (left) and Filter set 5 (BP 395-440, FT 460, LP 470) for fluorescence (right), with layers numbered (x500).

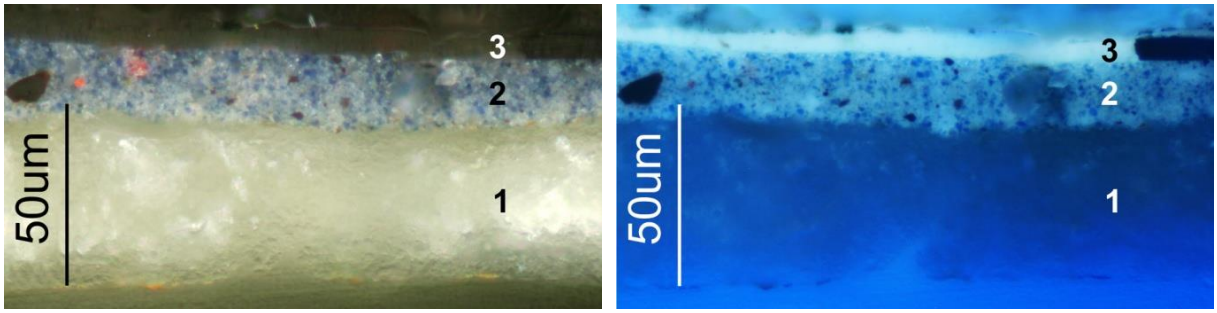


Figure IV.7 – Cross-section S6 (restoration), photographed in OM with normal (left) and UV light (right), with layers numbered (x500).

Appendix IV.4 – Pigments identification tables

Table IV.3 – Pigments identified in the preparatory layer

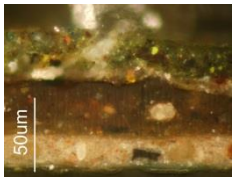
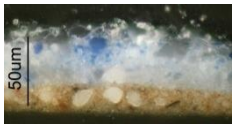
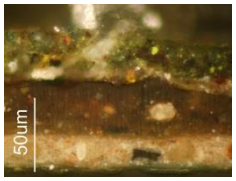
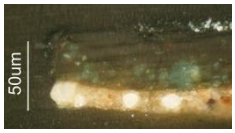
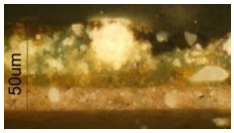
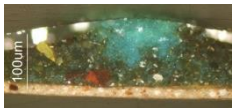
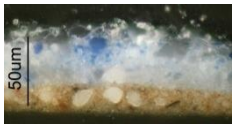
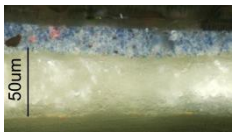
Preparatory layer						
Sample	**μ-EDXRF**	**PIXE**	**μ-Raman**		**Pigments identified & location in sample (layer no.)**	
			Wavenumber (cm^{-1})	Assignment		
S1 	-	Ca, Fe, Pb	101 (s) 662 (vw) 681 (vw) 830 (vw) 1051 (vs)	vs (CO_3^{2-})	**Lead White** $2PbCO_3.Pb(OH)_2$	1
			119 (vs) 148-149 (m) 220-224 (w) 312 (w) 388 (m) 480 (vw) 547 (vs)		**Red Lead** Pb_3O_4	1
			222 (m) [a, b, c, d] 296 (m) [a, b, c] 405 (m) [a, b, c, d]	δ_s (Fe-O)	**Iron Oxides,** possibilities: [a] Mars Orange/Red, Fe_2O_3; [b] Haematite, α-Fe_2O_3; [c] Sienna, Fe_2O_3 + MnO_2; [d] Red earths, Fe_2O_3 + clay + silica	1
S2 	-	Ca, Cu, Pb	828 (vw) 1047 (vs)		**Lead White** $2PbCO_3.Pb(OH)_2$	1
			1324-1326 (vs) 1598 (vs)	sp^3 (C-C) sp^2 (C-C)	**Carbon Black (?)** C	1
			1607 (s)		**Sienna (?)** Fe_2O_3 + MnO_2	1
S6 (restoration) 	-	n/a	154-155 (w) 280-281 (w) 710-711 (vw) 1084 (vs)		**Calcium Carbonate** $CaCO_3$	1

Table IV.4 – Pigments identified in the paint layers

Paint layers						
Sample	**μ-EDXRF**	**PIXE**	**μ-Raman**		**Pigments identified & location in sample (layer no.)**	
			Wavenumber (cm^{-1})	Assignment		
S1 	K, Ca, Ba, Cr, Fe, Co, Cu, Zn, Hg, Pb	S, Cl, Ca, Ti, Cr, Fe, Cu, Zn, Pb	138 (vs) 333 (w) 506 (w)		**Lead-Tin-Antimony Yellow** $Pb_2SnSbO_{6.5}$	3
			305 (vs) 607 (s)		**Cadmium Yellow** CdS	5
			411-414 (m) 617-620 (vw) 668-670 (vw) 1005 (s)	- v_s (SO_4^{2-})	**Gypsum (?)** $CaSO_4.2H_2O$	3
			1084 (vs)		**Calcium Carbonate** $CaCO_3$	3
			225-227(w) [a, b, c, d] 296 (w) [a, b, c]	- δ_s (Fe-O)	**Iron Oxides**, possibilities: [a] Mars Orange/Red, Fe_2O_3; [b] Haematite, α-Fe_2O_3; [c] Sienna, Fe_2O_3 + MnO_2; [d] Red earths, Fe_2O_3 + clay + silica	3

Paint layers						
Sample	**μ-EDXRF**	**PIXE**	**μ-Raman**		**Pigments identified & location in sample (layer no.)**	
			Wavenumber (cm^{-1})	Assignment		
			1325 (w, br)	sp^3 (C-C)	**Carbon Black (?)** C	5
S5 	K, Ca, Mn, Fe, (Ni), Cu, Pb	n/a	1094 (s)		**Azurite (?)** $2CuCO_3.Cu(OH)_2$	2
S3 	Sn, Ca, Mn, Fe, Cu, Pb	Ca, K, Fe, Cu, Si, Pb	n/a	n/a	n/a	-
S4 	K, Ca, Mn, Fe, Cu, Pb	S, Cl, Ca, Fe, Cu, Ti	151 (w) [e, f] 186 (w) [e, f] 404-409 (s) [f] 588-591 (m) [e]	δ (OCuO) - - -	[e] **Atacamite (?)** $Cu_2Cl.(OH)_3$ [f] **Paratacamite (?)** $Cu_2(OH)_3Cl$	2
S2 	K, Ca, Ba, Fe, (Ni), Cu, Pb	Si, S, Cl, Ca, Pb	256 (w) 543 (vs) 1088 (m) * 1350 (w)	δ (S_3^-) v_1 (S_3^-) v_1 (CO_3^{2-})	**Ultramarine Blue** $(Na,Ca)_8[(Al,Si)_{12}O_{24}](S,SO_4)$ (probably natural source due to the presence of calcite band, marked with asterisk)	2
			1051 (w)	v_s (CO_3^{2-})	**Lead White** $2PbCO_3.Pb(OH)_2$	2
S6 (restoration) 	K, Ca, Ba, Fe, (Ni), Cu, Pb	n/a	254-256 (w) 544 (vs) 1092-1095 (m) 1350-1356 (br) 1648 (br)	δ (S_3^-) v_1 (S_3^-) $2v_1$ (S_3^-) $3v_1$ (S_3^-)	**Ultramarine Blue** $(Na,Ca)_8[(Al,Si)_{12}O_{24}](S,SO_4)$ (probably synthetic source due to the absence of calcite bands)	2
			224 (w) 408 (m)	δ_s (Fe-O)	**Haematite (?)** α-Fe_2O_3	2

Appendix IV.5 – Analysis of selected cross-sections using PIXE

Note: in the following Figures IV.8 – IV.11 all the images are mirrored horizontally, and the area corresponding to the ground layer in the paint composite is outlined by white dots.

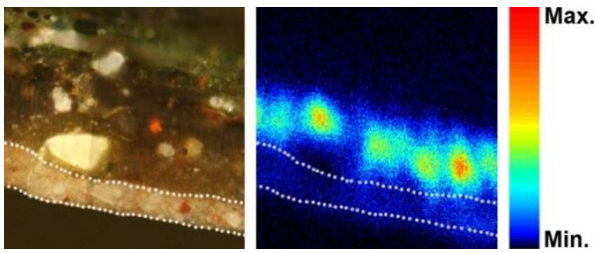


Figure IV.8 – OM image normal light (left) with corresponding Cu distribution map (right) of S1. μ-PIXE scale: 160μm x 160μm.

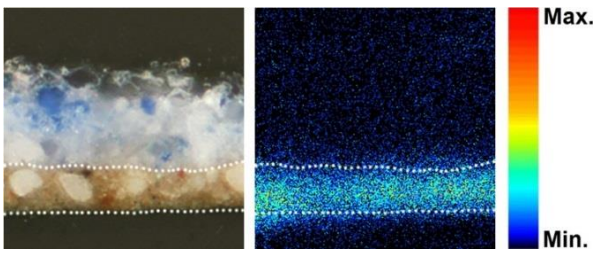


Figure IV.9 – OM image normal light (left) with corresponding Cu distribution map (right) of S2. μ-PIXE scale: 160μm x 160μm.

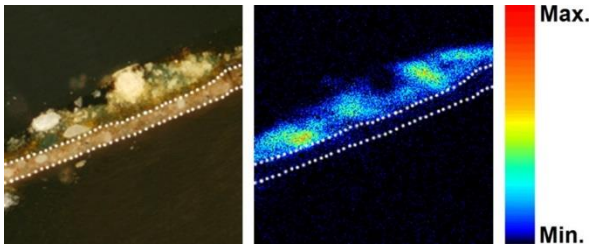


Figure IV.10 – OM image normal light (left) with corresponding Cu distribution map (right) of S3. µ-PIXE scale: 264µm x 264µm.

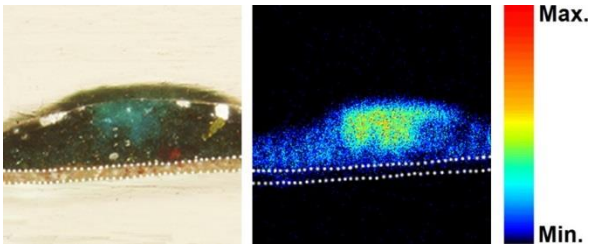


Figure IV.11 – OM image normal light (left) with corresponding Cu distribution map (right) of S4. µ-PIXE scale: 530µm x 530µm.

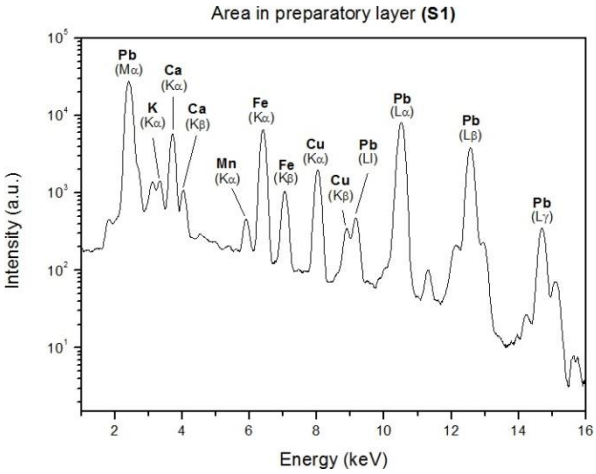


Figure IV.12 – µ-PIXE X-ray spectrum of raster area analyzed in the preparatory layer of S1.

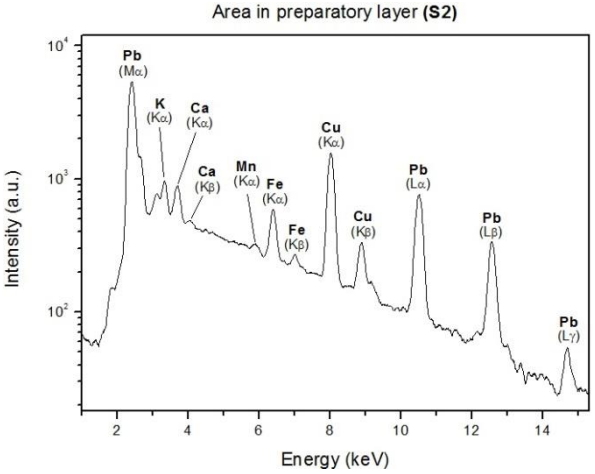


Figure IV.13 – µ-PIXE X-ray spectrum of raster area analyzed in the preparatory layer of S2.

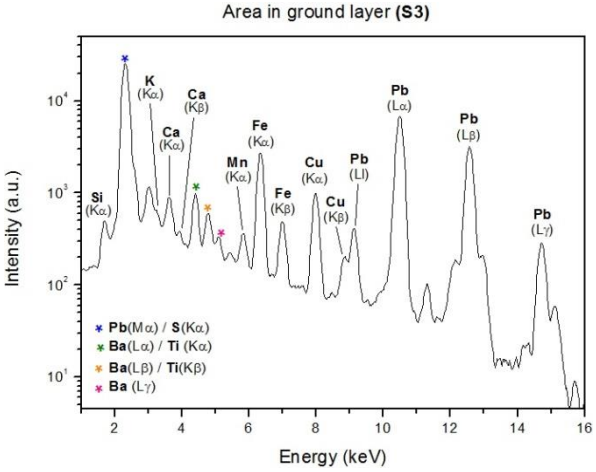


Figure IV.14 – µ-PIXE X-ray spectrum of raster area analyzed in the preparatory layer of S3.

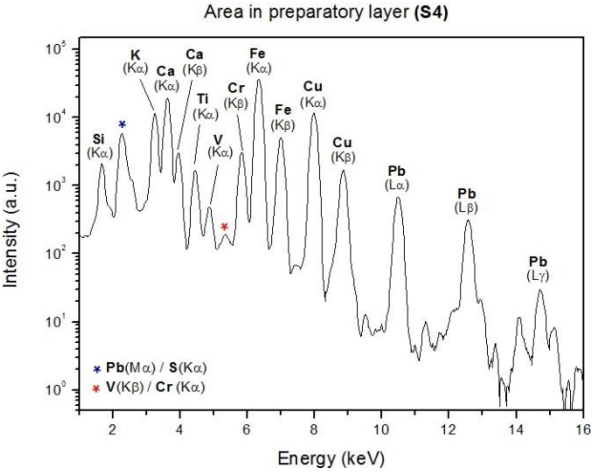


Figure IV.15 – µ-PIXE X-ray spectrum of raster area analyzed in the preparatory layer of S4.

Appendix IV.6 – Analysis of binder and varnish using µ-FTIR

Binder (see Fig. IV.16)

The illustrative spectrum to demonstrate analysis of the paint binder was acquired from a sample collected from the sky area (blue paint). The bands at **2927 cm^{-1}**, **2854 cm^{-1}** (CH_2 stretching), and **1708 cm^{-1}** (C=O stretching) indicate the presence of a drying oil [1; 2].The bands at **3536 cm^{-1}** (O-H stretching), **1403 cm^{-1}** (CO_3^{2-} asymmetric stretching), and **682 cm^{-1}** (CO_3^{2-} in plane rocking) are related to lead white ($2PbCO_3.Pb(OH)_2$), also detected by µ-Raman in the same blue layer (see Appendix IV.4, Table IV.4, S2) [2]. The intense band at **1010 cm^{-1}** (Si-O-Si and Si-O-Al overlapping stretching) reveals the other pigment present in the blue paint, ultramarine blue ($(Na,Ca)_8[(SO_4,S,Cl)_2|(AlSiO_4)_6]$), probably of natural source (lazurite, extracted from lapis-lazuli) [1]. FTIR also detected a band at **1535 cm^{-1}** (COO^- asymmetric stretching) which is indicative of a metal carboxylate, most probably a lead soap [3].

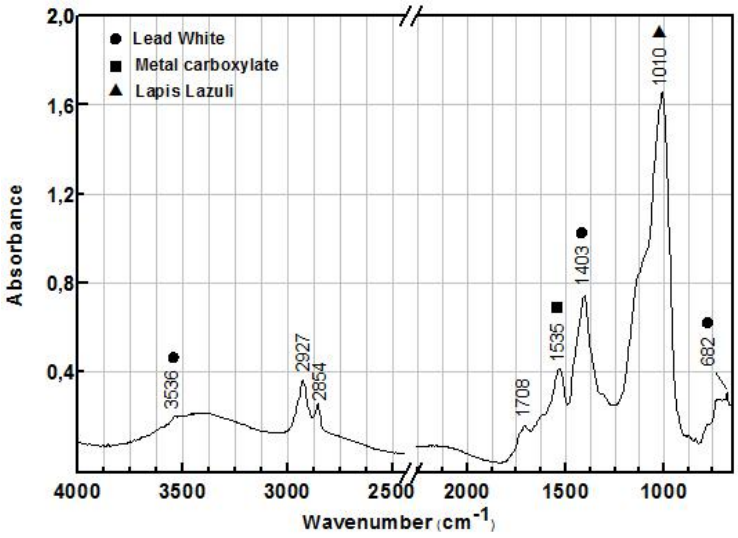


Figure IV.16 - µ-FTIR spectrum of paint sample.

Varnish (see Fig. IV.17)

The two strong and distinctive bands at **2954 cm^{-1}** and **2873 cm^{-1}** (CH stretching), and at **1716 cm^{-1}** (C=O stretching) indicate the presence of a triterpenoid resin, either dammar or mastic [1]. The remaining bands also indicative of this type of resin are between **1457** and **1384 cm^{-1}** (C-H bending); **1238** and **1045 cm^{-1}** (C-O stretching); and at **3436 cm^{-1}** (O-H stretching) [1].

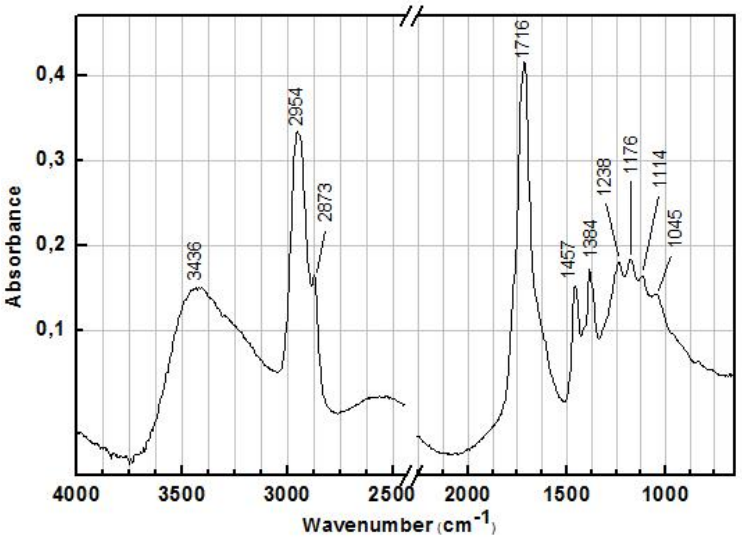


Figure IV.17 - µ-FTIR spectrum of varnish layer.

Appendix IV.7 – Analysis of interfacial layers using µ-FTIR and SEM/EDS

➢ **µ-FTIR**

Green translucid layer (see Fig. IV.18)

The distinctive bands at **2915 cm^{-1}** (CH_2 asymmetric stretching); **2850 cm^{-1}** (CH_2 symmetric stretching); **1589 cm^{-1}** (COO^- asymmetric stretching); and the less intense ones at **1469** cm^{-1} (CH_2 bending); **1442 cm^{-1}** (CH_2 bending); **1423 cm^{-1}** (COO^- symmetric stretching); and **1315 cm^{-1}** (CH_2 bending) all indicate a copper carboxylate [3; 4]. The band at **1712 cm^{-1}** (C=O stretching) indicates the presence of carboxylic acids within the oil matrix (formed during its drying process) [2].

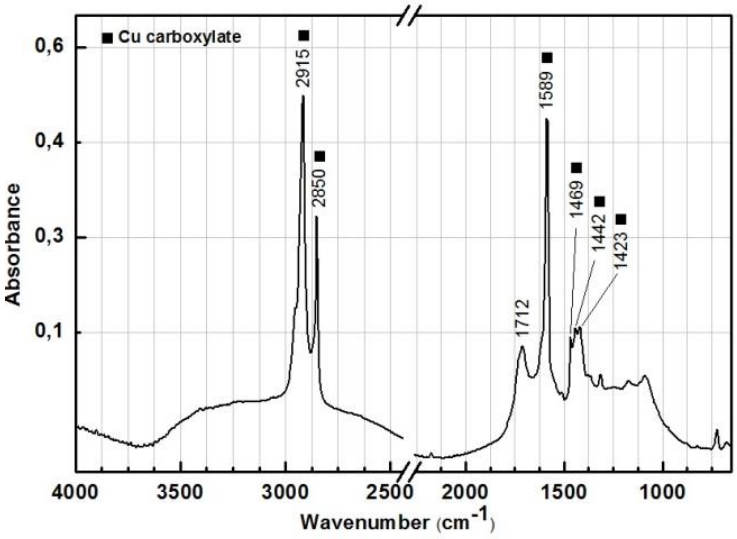


Figure IV.18 - µ-FTIR spectrum of green interfacial translucent layer.

White-grey layer covering Cu support (see Fig. IV.19)

The bands at **3536** cm^{-1} (O-H stretching), **1403** cm^{-1} (C-O stretching), **1049** cm^{-1} (CO_3^{2-} symmetric stretching), **836** cm^{-1} (CO_3^{2-} out of plane rocking), and at **682** cm^{-1} (CO_3^{2-} in plane rocking) all indicate the presence of lead white ($2PbCO_3.Pb(OH)_2$) [2]. The two distinctive bands at **2919** cm^{-1} and **2850** cm^{-1} (CH_2 stretching), indicate the presence of a drying oil [1], along with the ones at **1735 cm^{-1}** (C=O stretching of ester bond) and at **1091** cm^{-1} (C-O ester). The shift of the 1735 cm^{-1} band towards a lower wavenumber (from 1744 cm-1, the value of the same absorption for an unaged drying oil) indicates that this binder has aged at least through hydrolysis [5]. The band at **1515** cm-1 (COO^- asymmetric stretching) further indicates a metal carboxylate, most probably a lead soap [3].

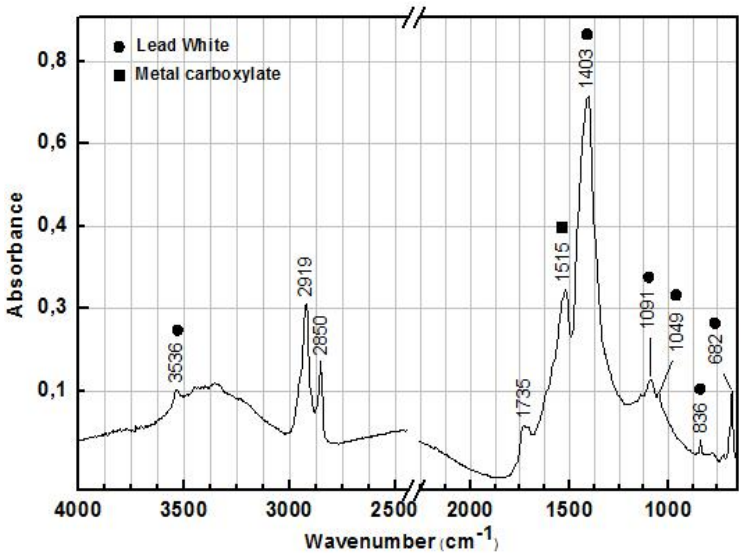


Figure IV.19 - µ-FTIR spectrum of white-grey layer found covering the copper support.

References used in Appendix IV.7:

[1] Derrick, M. R., Stulik, D., Landry, J. M. 1999. *Infrared Spectroscopy in Conservation Science, Scientific Tools for Conservation.* Los Angeles: Getty Conservation Institute.

[2] Campos, M. 2010. The study of lead White Oil Paints, A molecular approach to the whites of Amadeo de Souza-Cardoso. Master thesis, New University of Lisbon, Faculty of Sciences and Technology.

[3] Otero, V., Sanches, D., Montagner, C., Vilarigues, M., Carlyle, L., Lopes, J. A., Melo, M. J. 2014. Characterisation of metal carboxylates by Raman and infrared spectroscopy in works of art. *Journal of Raman Spectroscopy*, 45: 1197–1206.

[4] Robinet, L. & Corbeil, M.-C. 2003. The Characterization of Metal Soaps. *Studies in Conservation*, 48: 20-40.

[5] Pedroso, J. 2009. Estudo da degradação de óleos secativos, em tintas de Amadeo de Souza-Cardoso, Silva Porto e Gustave Courbet. Master thesis, New University of Lisbon, Faculty of Sciences and Technology.

➢ **SEM/EDS**

Figure IV.20 – OM image of the underside of paint fragment with normal light (left) and Filter set 5 (BP 395-440, FT 460, LP 470) for fluorescence (right) (x50). Note the transparent layer fluorescing on the right.

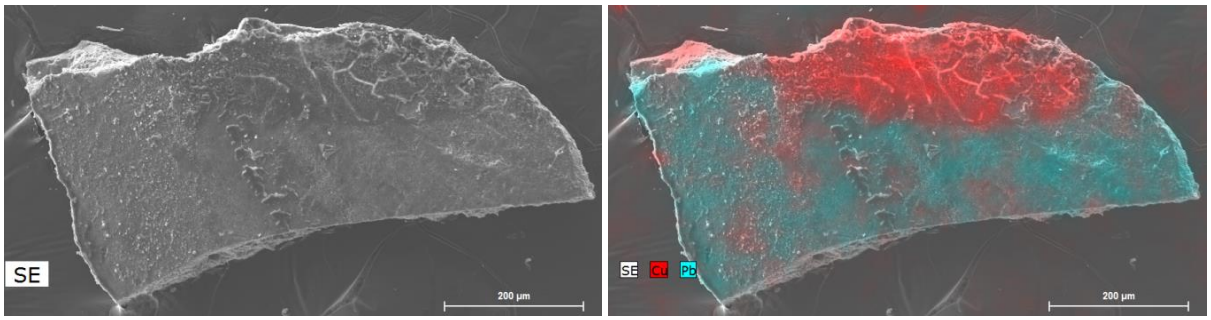


Figure IV.21 – SE image of the underside of paint fragment (left) and elemental distribution map, with Cu (red) and Pb (blue) (right).

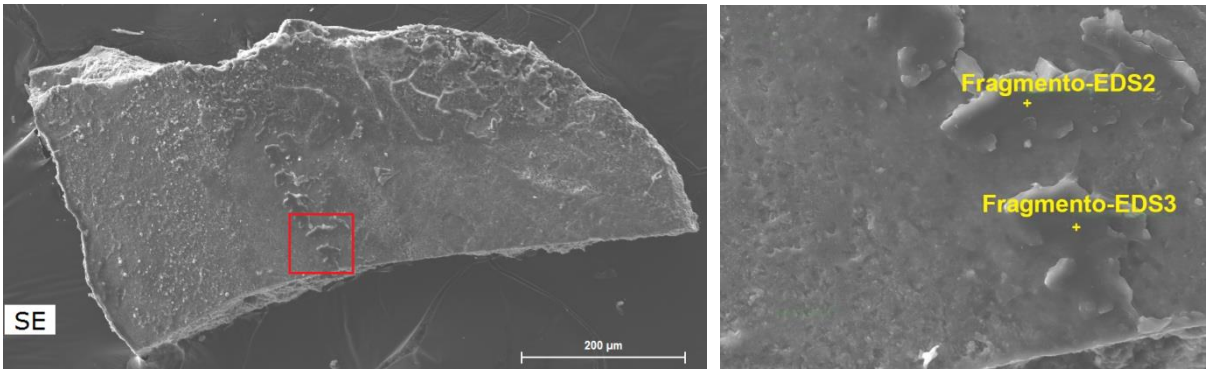


Figure IV.22 – Map of the areas analysed in the transparent layer ("Fragmento-EDS 2" and "Fragmento-EDS 3").

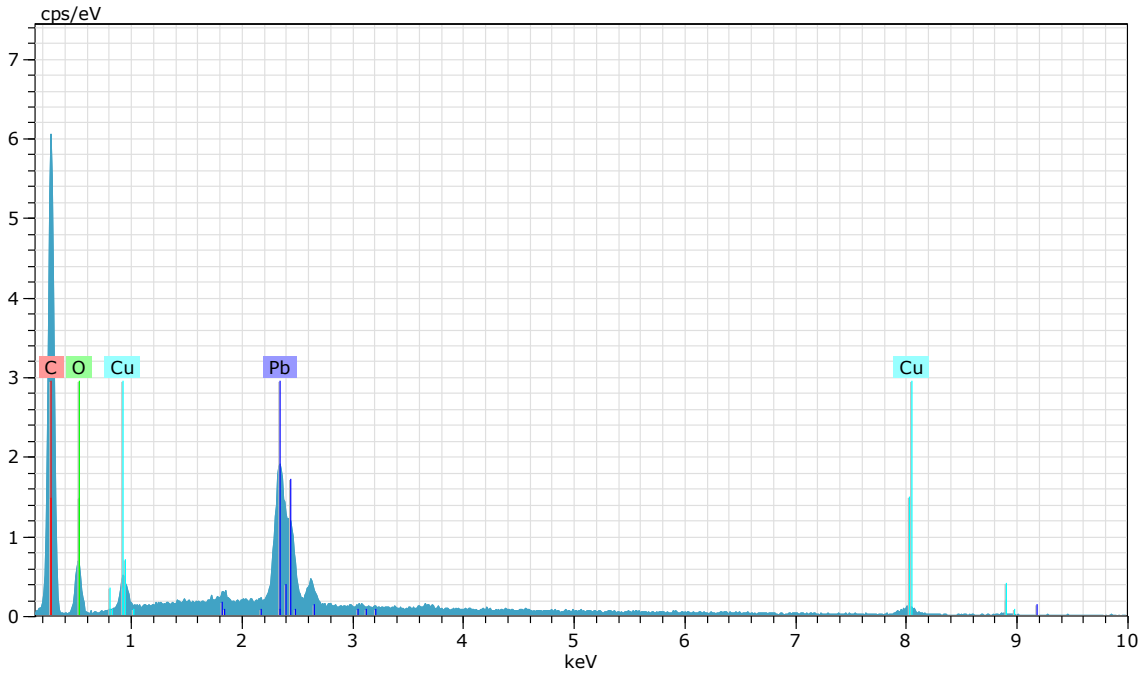


Figure IV.23 – EDS spectrum for the first area analysed in the transparent layer (“Fragmento-EDS 2”).

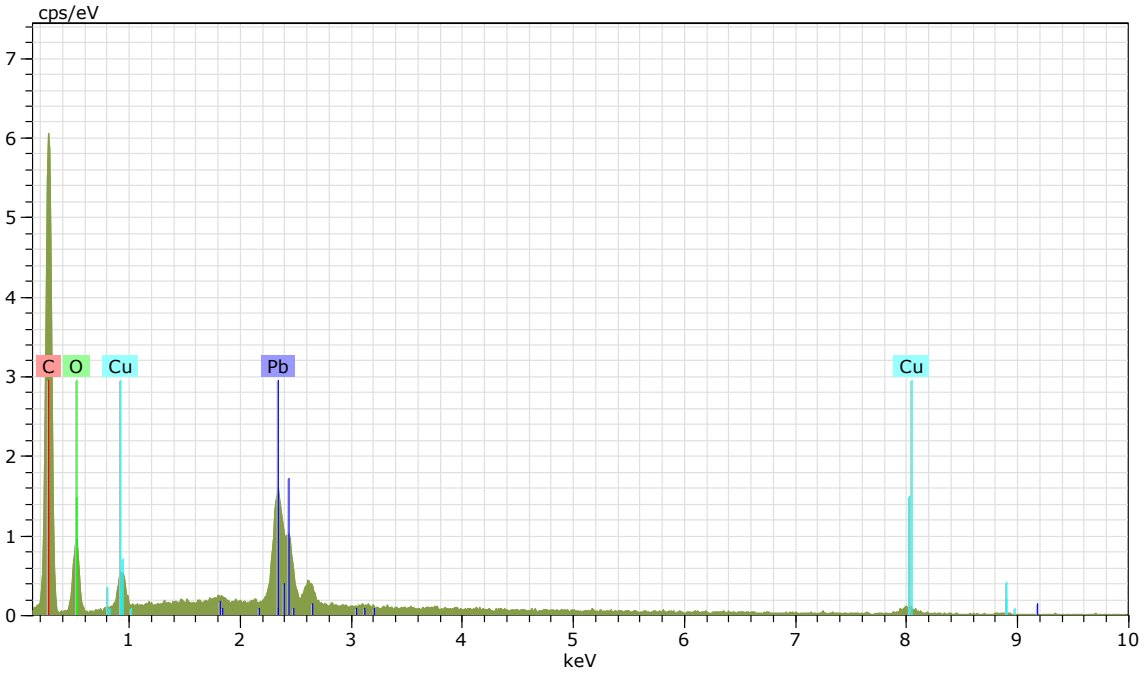


Figure IV.24 – EDS spectrum for the second area analysed in the transparent layer (“Fragmento-EDS 3”).

Appendix IV.8 – Elemental characterization of the copper plate using µ-EDXRF

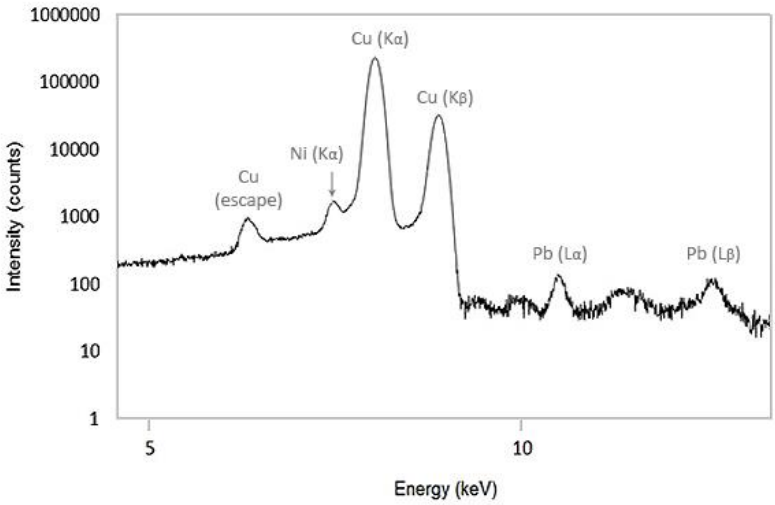


Figure IV.25 - Illustrative µ-EDXRF spectrum of the painting's copper support.

Appendix V – Scientific investigation

Appendix V.1 – Horovitz's conclusions from 1986 and 1996 study on consolidants & results of Pilot-project to determine the choice of consolidants and their concentration

Table V.1 – Summary of Horovitz's assessments for each consolidant in 1986 [1] and 1996 [2]

Consolidant (water based highlighted in blue)	**Ingredients of brand-name consolidants**	**Assessments reported in 1986** (directly quoted from [1], p. 47)	**Assessments reported in 1996** (directly quoted from [2], p. 279)		
			Visible reaction	**Adhesion**	**Handling**
Gelatine	-	'Very poor adhesion with copper'	'No discoloration of film but slight change in colour of copper beneath'	'None'	'Cools quickly on contact with copper'
Isinglass	-	*Not included*	'As gelatine'	'Negligible'	'As gelatine'
Sturgeon glue + 50% honey	-	*Not included*	'No change noted but glue is yellow'	'Good initially but detached after three weeks'	'As gelatine'
Mowilith DMC2	PVA emulsion [2] based on copolymer VA/maleate [3]	*Not included*	'Green/black'	'Good'	'Strong surface tension, poor flow on copper'
Vinamul 3252	EVA dispersion [2] based on copolymer VA/ethylene copolymer [3]	*Not included*	'Green tinge'	'Very good'	'Satisfactory'

Consolidant (water based highlighted in blue)	**Ingredients of brand-name consolidants**	**Assessments reported in 1986** (directly quoted from [1], p. 47)	**Assessments reported in 1996** (directly quoted from [2], p. 279)		
			Visible reaction	**Adhesion**	**Handling**
Plextol B500	Acrylic dispersion [4] based on copolymer EA/MMA (66% EA) [3]	'Turned green within periods ranging from 30 minutes to two weeks'	'Green tinge Aged sample: green tinge'	'Good Aged sample: peeled up'	'Film shrinkage occurred'
Mastic + 10% stand oil	-	*Listed but not mentioned*	'No change Aged mastic sample: greeny yellow'	'Good'	'Good flow due to turpentine dilution'
Lascaux wax	-	*Not included*	'Mildly yellow'	'Good'	'Tacky, poor flow'
Wax-resin (*)	-	*Not included*	'Turning yellow'	'Good'	'Bulky'
Beeswax	-	'Turned green within periods ranging from 30 minutes to two weeks'	'Aged sample: vividly green, crusty corrosion beneath'	'Lifting'	'Bulky'
Beva 371	Elvax 150, AC400, Ketone N, paraffin wax + Cellolyn 21 [1]	'Appeared to adhere well to the copper and no reactions were noted'	'Whitish, opaque Aged sample: unchanged'	'Very good Aged sample: unchanged'	'Relatively bulky, tacky, solvent and heat required'
Bedacryl 122X	Acrylic adhesive based on homopolymer BMA [3]	'Appeared to adhere well to the copper and no reactions were noted'	'Aged sample clear'	'Aged sample: very good'	'Solvent concentration difficult to determine'
Plexisol P550	Acrylic adhesive based on homopolymer BMA [3]	'Turned green within periods ranging from 30 minutes to two weeks'	'No change Aged sample: unchanged'	'Good Aged sample: still soft (low T_g)'	'As above'
Mowilith 20 or Mowilith AYAB	PVA solvent solution [1]	'Appeared to adhere well to the copper and no reactions were noted'	'No change Aged sample: unchanged'	'Good Aged sample: unchanged'	'As above'
Paraloid B-72	Acrylic adhesive based on copolymer EMA/MA (70/30) [3]	'Appeared to adhere well to the copper and no reactions were noted'	'No change Aged sample: unchanged'	'Excellent Aged sample: unchanged'	'Solvent concentration difficult to determine'
Paraloid B-48 S	Acrylic adhesive based on copolymer BA/MMA (20-44% BA) [3]	*Not included*	'No change'	'Excellent'	'As above. Stringy when viscous'

Consolidant (water based highlighted in blue)	Ingredients of brand-name consolidants	Assessments reported in 1986 (directly quoted from [1], p. 47)	Assessments reported in 1996 (directly quoted from [2], p. 279)		
			Visible reaction	Adhesion	Handling
Paraffin wax mixtures (**)	-	'Very poor adhesion with copper '	*Not re-evaluated*		
Celaton	n-hydroxy methyl nylon [1]	'Very poor adhesion with copper'	*Not re-evaluated*		
Primal AC634	Acrylic dispersion based on copolymer MMA/EA (65/35) [4]	'Turned green within periods ranging from 30 minutes to two weeks'	*Not re-evaluated*		
Vynamul 6816	PVA emulsion [1]	'Turned yellow after one hour'	*Not re-evaluated*		

(*) Information about which type of wax, resin, and the proportion of one to another is not given.
(**) Information about other ingredients and proportions in the mixtures is not given.

References for Table V.1:

[1] Horovitz, I. 1986. Paintings on copper supports: techniques, deterioration, and conservation. *The Conservator*, 10: 44-8.

[2] Horovitz, I. 1996. The Consolidation of Paintings on Copper Supports. In: J. Bridgland, ed. ICOM *Committee for Conservation, 11th Triennial Meeting, Preprints*. London: James & James, pp. 276-81.

[3] Down, J. 2015. The evaluation of selected poly(vinyl acetate) and acrylic adhesives: A final research update. *Studies in Conservation*, 60(1): 33-54.

[4] Horie, C. V. 2010. *Materials for Conservation: Organic Consolidants, Adhesives and Coatings*, 2nd ed. Oxford: Butterworth-Heinemann.

Table V.2 – Results of Pilot-project to determine the choice of consolidant and concentration

Consolidant/Solvent	Concentration		Results	Observations
Beva 371b in toluene	High	1:1 (v/v)	✓	Good adhesion.
	Medium	1:3 (v/v)	✓	Good adhesion.
	Low	1:39 (v/v)	✘	Immediate failure due to lack of tack.
Laropal A 81 in Shellsol D40 + Shellsol A (6:4)	High	80% (w/v)	✓	Good adhesion.
	Medium	30% (w/v)	✓	As above.
	Low	20% (w/v)	✓	As above.
Mowilith 20 in toluene	High	40% (w/v)	✓	Good adhesion.
	Medium	15% (w/v)	✓	As above.
	Low	5% (w/v)	✓	As above.

Consolidant/Solvent	Concentration		Results	Observations
Paraloid-44 in xylene	High	40% (w/v)	✓	Good adhesion.
	Medium	15% (w/v)	✘	Failure due to consolidant adhering to paint fragment alone and not to copper substrate.
	Low	5% (w/v)	✘	Failure due to lack of tack. Film still soft at the edges after 24 hours.
Paraloid B-67 in White Spirits	High	40% (w/v)	✓	Good adhesion.
	Medium	15% (w/v)	✘	Failure, apparently due insufficient amount of consolidant underneath paint fragment
	Low	5% (w/v)	✘	Failure due to lack of tack.
Paraloid B-72 in toluene	High	40% (w/v)	✓	Good adhesion.
	Medium	15% (w/v)	✓	Good adhesion.
	Low	5% (w/v)	✘	Failure, apparently due insufficient amount of consolidant underneath paint fragment
Regalrez 1094 in Shellsol D40	High	80% (w/v)	✘	Still sticky after left to dry for 48 hours.
	Medium	-	-	-
	Low	-	-	-

Detailed information about paint fragments used in Pilot-Project:

Identification code of drawdown: PPBP 2.5g BP (K+L) + 16 drops Min. Spirits **/ Date**: 25/02/2011

Composition & details: the paint drawdown belongs to the Oil Paint Rheology Project (OPRP), sample PPBP-MS-0.5 which was prepared and applied to Melinex® using a brush. The paint (Pilot Project Base Paint, PPBP), consisted of Kremer Pigmente Lead White (K), 12.4g, and Cornelissen's Prussian Blue, FCT Stock (P), 0.2g which was hand ground (granite slab & muller) with 3.11g of AH2 Linseed oil. AH2 consists of 200ml linseed oil extracted from Turkish seeds (by Pedro Alves, Tate 2009) heated to 150C with 100g lead (II) oxide on 15.10.2010. To the base paint was added by mineral spirits by drops, to approximately 0.5% by weight of the base paint.

Identification code of drawdown: EP 13.8 SWAC4-12-15 **/ Date:** 17/08/04

Composition & details: the paint drawdown belongs to the HART Project. It was applied in the same day it was made to a polyester film (Melinex®) using a fixed distance applicator (90 microns thickness). The paint was hand-ground on a granite slab/granite muller, with 10.6g washed stack process lead white (code SWA), with 15% by weight (1.88g) Omya 'A' Chalk, no grinding or flow agents (sample received 2003, code C4), in 1.5g linseed oil (Electra seeds 1999 stock, extracted March 2003). Further details on materials and suppliers available in the HART Project Report, L. Carlyle, DCR-UNL.

Appendix V.2 – Table with relevant chemical & physical properties and comments on stability of chosen consolidants

Note: substances in **bold** and highlighted in light grey are the ones chosen for study.

Table IV.3 – Relevant chemical & physical properties and comments on stability of chosen consolidants

Brand name	Chemical classification & composition	T_g (ºC)	Solubility	Ageing characteristics	Common conservation use	Other observations	Supplier
Paraloid B-44	Thermoplastic acrylic resin based on EA/MMA copolymer [1]	60 [2]	Good: toluene; xylene; selected esters; acetone; methyl ethyl ketone [2] Limited: most alcohols and aliphatic hydrocarbons [2]	Ageing tests have shown that it suffers from chain-scission processes and cross-linking reactions [3]	Used in Incralac [4]; suited for treated metal, copper, zinc, brass, treated aluminum, concrete floors, and certain plastics [2]	Provides an outstanding combination of hardness, flexibility, and adhesion to various substrates. [2]	Dow Chemical Company
Paraloid B-67	Thermoplastic acrylic resin based on iBMA homopolymer [1]	50 [5]	Good: toluene; xylene; acetone; petroleum benzine; turpentine; mineral spirits; [6] Limited: ethanol [6]	Ageing tests have revealed that it suffers from extensive cross-linking [6; 4] on exposure to heat and ultraviolet radiations, even under normal gallery conditions. As cross-linking occurs, it becomes increasingly insoluble [6].	Used as a varnish [6]; when combined with medium and long-oil alkyds, drying oils, and oleoresinous varnishes, it provides coatings with improved hardness, faster drying speed, and better retention of colour and gloss result, and hold out and brushing characteristics are also improved [5]	It is a very hydrophobic polymer, providing excellent water resistance [5]; it is particularly compatible with medium and long-oil alkyds, drying oils, and oleoresinous varnishes [5]	Dow Chemical Company
Paraloid B-72	Thermoplastic acrylic resin based on EMA/MA copolymer (70:30) [1]	40 [7]	Good: toluene; xylene; acetone; carbon tetrachloride; Methyl Ethyl Ketone; ethanol [8]	Ageing tests have demonstrated that it is extremely stable [7] and has very good ageing	Used as a varnish; consolidant for paint, wood, plaster, stone and ethnographic objects; adhesive for	Unique in possessing a high tolerance for ethanol [7]	Dow Chemical Company

Brand name	Chemical classification & composition	T_g (ºC)	Solubility	Ageing characteristics	Common conservation use	Other observations	Supplier
			Limited: isopropanol [8]	properties: it remains colourless and soluble in the solvent sin which it was originally dissolved extrapolated to 200 years under normal gallery conditions [6]; however it may decrease its intrinsic viscosity upon exposure to UV light, which indicates a decrease in molecular weight owing to chain-scission (rather than cross-linking) [6]	ceramics and glasses; fixative for pencil, charcoal, chalk drawings and pastels; inpainting medium [6]		
Mowilith 20	PVA resin based on low molecular weight solid VA homopolymer [9]	36 ± 2 [9]	Good: ethanol (+ 5% water); ethyl acetate; butyl acetate; acetone; methyl ethyl ketone; toluene; xylene [10] Limited: ethanol (anhydrous) [10]	It is considered to be chemically stable [11], as PVA is a resin showing excellent ageing properties, highly resistant to deterioration at normal temperatures and not hydrolysing [6]	PVA is used in dispersion to make glues for paper, textiles, leather, wood, etc. [10]; and as a consolidant [6]	Because the PVA T_g may be close to room temperature, depending on the molecular weight selected, it can be prone to dirt retention (Mowilith 20 has the lowest molecular weight from the range of PVA's that is sold) [12]	Farberwerke Hoechst AG (in Europe)
Beva 371b	Resin based on copolymer ethylene/VA [1] Detailed composition:	(*)	Good: hydrocarbon solvents (VMP naptha, toluene, etc.) [13]	Stable both thermally and chemically [13]; studies for Beva 371 showed that it remains flexible after	Consolidant for pictorial layers	Ensures good adhesion to various substrates, including metal; strong and flexible	Conservation Support Systems

Brand name	Chemical classification & composition	T_g (ºC)	Solubility	Ageing characteristics	Common conservation use	Other observations	Supplier
	60% solvents: toluene and naphta + 40% solids: two ethylene vinyl acetate copolymers (Elvax 150 resin, and A-C Copolymer 400), an aldehyde ketone resin, phthalate ester of hydroabietyl alcohol (Cellolyn 21) and paraffin wax [13]			ageing and that it yellows [1]		that may be used hot or cold in various dilutions and can be heat activated after application [12]	
Laropal A 81	Low molecular weight aldehyde resin [14], formed through a condensation reaction between urea, formaldehyde and aliphatic aldehyde (isobutyraldehyde) [15]	57 [14]	Needs to be dissolved in a mixture of aliphatic and aromatic (30-40% content) of solvents; soluble in most oxygenated solvents (ketones, alcohols, ethers); it will also dissolve in fast-evaporating cycloparaffins [15]	Material with photochemical and heat stability [14]; ageing tests have shown that slight changes in polarity may occur, although it still remains soluble in same solvents in which it was initially dissolved [15]	Used in combination with other resins to make coatings [14]; production of all-purpose pigment pastes [14]	It was introduced to replace the less stable ketone resins such as Laropal K-80. [12]; used in Gamblin Conservation Colors	BASF
Regalrez 1094	Low molecular weight hydrocarbon resin [16], formed by hydrogenated oligomer of styrene and alpha-methyl styrene. [6]; produced by polymerization and hydrogenation of pure monomer hydrocarbon feedstocks [16]	40 [16]	Good: aliphatic and aromatic solvents; C5 and higher esters and ketones [16]; also soluble in non-aromatic, non-polar solvents [12]	Ageing testes have showed that it is a highly stable material [16] if stabilized with Tinuvin 292 [12]; does not become insoluble due to cross-linking [6]; does not yellow [6]. If not stabilized, it ages to become extremely embrittled [6]	Use as a picture varnish [conservation easel]; in adhesives [16]	Contains no added antioxidants or UV stabilizers [9]; has been reported to remain sticky in varnishes [12], and that is thought to happen due to the possibility of Regalrez needing a slightly longer time to dry due to its affinity to non-polar solvents [12]	Hercules Corporation

(*) Activation temperature = 65ºC [13]

References for Table IV.3:

[1] Down, J. 2015. The evaluation of selected poly(vinyl acetate) and acrylic adhesives: A final research update. *Studies in Conservation*, 60(1): 33-54.

[2] Rohm & Haas product information sheet for “PARALOID™ B-44 100%”.

[3] Lazzari, M. & Chiantore, O. 2000. Thermal-ageing of Paraloid acrylic protective polymers. *Polymer,* 41: 6447-6455.

[4] Horie, C. V. 2010. *Materials for Conservation: Organic Consolidants, Adhesives and Coatings*, 2nd ed. Oxford: Butterworth-Heinemann.

[5] Rohm & Haas product information sheet for “PARALOID™ B-67 100%”.

[6] Jill Whitten, Barbara A. Buckley, Helen Houp, Lydia Vagts, Harriet Irgang, Mark van Gelder, Susan S. Blakney, Nina A. Roth-Wells and Gianfranco Pocobene. “V. Polymeric Varnishes” [accessed 15 August 2015] Available at: <http://www.conservation-wiki.com/wiki/V._Polymeric_Varnishes#ref55>

[7] Rohm & Haas product information sheet for “PARALOID™ B-72 100%”.

[8] Conservation and Art Material Encyclopaedia Online (Cameo) [accessed 14 July 2015] Available at <http://cameo.mfa.org/wiki/Paraloid@_B-72>

[9] Kremer product information sheet for “Polyvinyl Acetate 20”.

[10] Kremer product information sheet for “Polyvinyl Acetates 20, 30, 50”.

[11] Kremer Material Safety Data Sheet (MSDS) for “Polyvinyl Acetate 20”

[12] J. H. Stoner & R. Rushfield (editors) *Conservation of Easel Paintings.* United Kingdom: Routledge.

[13] http://www.conservationsupportsystems.com/system/assets/msds/New_Beva_Formula

[14] BASF product information sheet for “Laropal® A 81”.

[15] Reddington, S. 2015. Laropal 81 as an alternative to MS2A and other resins. In: A. Barros D’Sa, L. Bone, R. Clarricoates, & H. Dowding, eds. *Current Technical Challenges in the Conservation of Paintings.* London: Archetype Publications Ltd., p. 54-68.

[16] Kremer product information sheet for “Regalrez ® 1094 Hydrocarbon Resin”.

Appendix V.3 – Organization of experiment samples

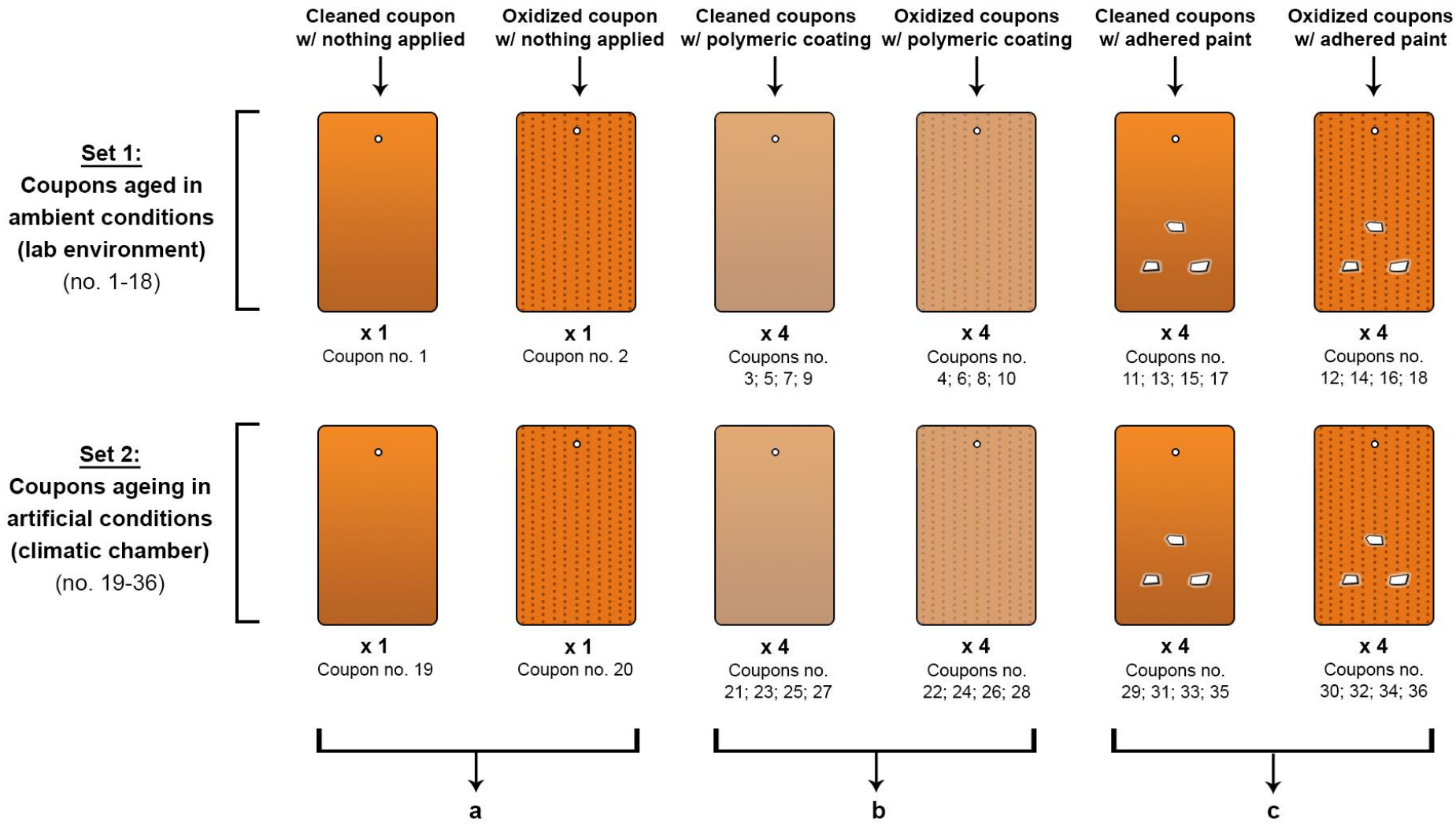


Figure V.1 – Diagram with organization of experiment samples.

Table V.4 – Organization of experiment samples

Coupon number	**Copper surface** (cleaned/oxidized)	**Ageing conditions** (Set 1/ Set 2)	**Processing** (a, b, c)	**Detailed description**	**Coupon identification code**
1	Cleaned	Set 1	a	Control coupons with nothing applied	**1. C-Set 1-a**
2	Oxidized	Set 1	a		**2. O-Set 1-a**
3	Cleaned	Set 1	b	Coating of Paraloid B-72 15% in xylene (w/v)	**3. C-Set 1-b-B72**
4	Oxidized	Set 1	b		**4. O-Set 1-b-B72**
5	Cleaned	Set 1	b	Coating of Mowilith 20 10% in toluene (w/v)	**5. C-Set 1-b-MOW**
6	Oxidized	Set 1	b		**6. O-Set 1-b-MOW**
7	Cleaned	Set 1	b	Coating of Laropal A81 20% in mixture of Shellsol D40 + Shellsol A (6:4) (w/v)	**7. C-Set 1-b-LAR**
8	Oxidized	Set 1	b		**8. O-Set 1-b-LAR**
9	Cleaned	Set 1	b	Coating of Beva 371b in toluene 1:3 (v/v)	**9. C-Set 1-b-BEV**
10	Oxidized	Set 1	b		**10. O-Set 1-b-BEV**
11	Cleaned	Set 1	c	3 paint fragments* adhered with Paraloid B-72 15% in xylene (w/v)	**11. C-Set 1-c-B72**
12	Oxidized	Set 1	c		**12. O-Set 1-c-B72**
13	Cleaned	Set 1	c	3 paint fragments* adhered with Mowilith 20 10% in toluene (w/v)	**13. C-Set 1-c-MOW**
14	Oxidized	Set 1	c		**14. O-Set 1-c-MOW**
15	Cleaned	Set 1	c	3 paint fragments* adhered with Laropal A81 20% in mixture of Shellsol D40 + Shellsol A (6:4) (w/v)	**15. C-Set 1-c-LAR**
16	Oxidized	Set 1	c		**16. O-Set 1-c-LAR**
17	Cleaned	Set 1	c	3 paint fragments* adhered with Beva 371b in toluene 1:3 (v/v)	**17. C-Set 1-c-BEV**
18	Oxidized	Set 1	c		**18. O-Set 1-c-BEV**
19	Cleaned	Set 2	a	Control coupons with nothing applied	**19. C-Set 2-a**

Coupon number	**Copper surface** (cleaned/oxidized)	**Ageing conditions** (Set 1/ Set 2)	**Processing** (a, b, c)	**Detailed description**	**Coupon identification code**
20	Oxidized	Set 2	a		**20. O-Set 2-a**
21	Cleaned	Set 2	b	Coating of Paraloid B-72 15% in xylene (w/v)	**21. C-Set 2-b-B72**
22	Oxidized	Set 2	b		**22. O-Set 2-b-B72**
23	Cleaned	Set 2	b	Coating of Mowilith 20 10% in toluene (w/v)	**23. C-Set 2-b-MOW**
24	Oxidized	Set 2	b		**24. O-Set 2-b-MOW**
25	Cleaned	Set 2	b	Coating of Laropal A81 20% in mixture of Shellsol D40 + Shellsol A (6:4) (w/v)	**25. C-Set 2-b-LAR**
26	Oxidized	Set 2	b		**26. O-Set 2-b-LAR**
27	Cleaned	Set 2	b	Coating of Beva 371b in toluene 1:3 (v/v)	**27. C-Set 2-b-BEV**
28	Oxidized	Set 2	b		**28. O-Set 2-b-BEV**
29	Cleaned	Set 2	c	3 paint fragments* adhered with Paraloid B-72 15% in xylene (w/v)	**29. C-Set 2-c-B72**
30	Oxidized	Set 2	c		**30. O-Set 2-c-B72**
31	Cleaned	Set 2	c	3 paint fragments* adhered with Mowilith 20 10% in toluene (w/v)	**31. C-Set 2-c-MOW**
32	Oxidized	Set 2	c		**32. O-Set 2-c-MOW**
33	Cleaned	Set 2	c	3 paint fragments* adhered with Laropal A81 20% in mixture of Shellsol D40 + Shellsol A (6:4) (w/v)	**33. C-Set 2-c-LAR**
34	Oxidized	Set 2	c		**34. O-Set 2-c-LAR**
35	Cleaned	Set 2	c	3 paint fragments* adhered with Beva 371b in toluene 1:3 (v/v)	**35. C-Set 2-c-BEV**
36	Oxidized	Set 2	c		**36. O-Set 2-c-BEV**

Meaning of identification codes: **C** = Cleaned copper surface; **O** = Oxidized copper surface; **Set 1** = Coupons aged in ambient conditions (control); **Set 2** = Coupons aged in climatic chamber; **a** = Coupons with nothing applied/bare copper; **b** = Coupons with consolidant coating; **c** = Coupons with adhered paint fragments; **B72** = Paraloid B-72; **MOW** = Mowilith 20; **LAR** = Laropal A 81; **BEV** = Beva 371b.

*** Detailed information about paint fragments:**

Identification code of drawdown: EP 13.8 SWAC4-12-15 **/ Date:** 17/08/04

Composition & details: the paint drawdown belongs to the HART Project. It was applied in the same day it was made to a polyester film (Melinex®) using a fixed distance applicator (90 microns thickness). The paint was hand-ground on a granite slab/granite muller, with 10.6g washed stack process lead white (code SWA), with 15% by weight (1.88g) Omya 'A' Chalk, no grinding or flow agents (sample received 2003, code C4), in 1.5g linseed oil (Electra seeds 1999 stock, extracted March 2003). Further details on materials and suppliers available in the HART Project Report, L. Carlyle, DCR-UNL.

Appendix V.4 – Description of experimental procedure

Step 1. Fabrication of the copper coupons

Thirty six coupons with the dimensions of 2.5 x 1.5 x 0.7 cm were cut from a copper plate using a 3/0 jeweler's saw blade. All four corners and edges of the coupons were rounded with files and sandpaper to eliminate any sharp burrs. A number ranging from 1 to 36 was assigned to each coupon, and engraved by hand on the top right corner with a sharp metal point. A small hole (1 mm of diameter) centered and close to the top edge was drilled into every coupon using a Dremel machine (see Appendix VI, Equipment & Suppliers), so that the coupons could be suspended on cotton strings for oxidizing and when being immersed in the consolidant solution for application of the polymeric coatings under study (Steps 3 and 4 below).

Step 2. Cleaning and polishing

The coupons which went into the kiln (see Appendix VI, Equipment & Suppliers) to be oxidized in a controlled environment were previously polished and degreased, in order to have a freshly-cleaned surface of metallic copper as a base for the growth of new oxide layers on top.

This was achieved by progressively polishing both front and back of the coupons with a series of Micro-Mesh sheets of increasing grit (6000→8000→12000), both in a vertical and horizontal direction. This method was preferred to cleaning the surfaces with a paste of calcium carbonate in distilled water, since polishing clothes avoided contact of water with the copper, thereby preventing any chances of accelerated oxidation processes.

Once polished to a mirror-like finishing, the surfaces of the coupons were degreased, to remove any grease from the rolling machine used to achieve the desired thickness, and from working the coupons with the fingers while sawing and polishing. This was done gradually by rubbing the coupons with cotton swabs dipped in three 100% pure solvents, employed by order of increasing polarity: White Spirit → dichloromethane → acetone.

Those intended to be used as "clean" coupons received coatings or had the paint fragments adhered immediately after being cleaned in order to avoid oxidation.

Step 3. Oxidation in a controlled environment

Two rows of previously cleaned coupons (Step 2) were made by passing a 100% cotton string through the holes previously made with the Dremel, making knots in between each coupon so that they would not slide on the string and touch each other when suspended. A domestic glass cooking pot with a glass lid was cleaned on the inside using lab detergent, then rinsed with distilled water. The rows of coupons were hung lengthwise, being held at both ends on the outside of the glass container with autoclave tape (see Appendix VI, Equipment & Suppliers). The bottom of the container was carefully filled with distilled water using a glass pipette so that no water touched the copper coupon surfaces. The lid was put on, and then sealed with more autoclave tape. The glass container was then put inside a kiln (see Appendix VI, Equipment & Suppliers) with the temperature being set at 60ºC, where it remained for a total of 23 days.

After taking out the coupons from the glass container and before using them, they were put to rest on a glass support, uncovered, inside the kiln for one hour at the same temperature to ensure thorough drying by evaporation of any remaining water molecules on their surfaces.

Step 4. Applying polymeric coatings & adhering oil paint fragments

Polymeric coatings

Under a laboratory solvent extractor, the coupons were immersed fully in the consolidants which were each in clean glass bottles filled to a depth to allow full coverage of each coupon. Immersion was the chosen method for coating the coupons (rather than brushing or spraying) due to being considered by the PROMET project the one method which allows to achieve the most uniform and continuous coating [32-34]. Coupons were suspended from a hook made of copper wire placed through the central hole at the top of each coupon. Immediately after dipping they were placed to dry horizontally, resting between two glass slides which made contact only at the top and the bottom edges on the back surface of each coupon. By drying horizontally significant differences in the thickness of the coatings were avoided, and air circulation was ensured.

Immediately after immersion, the coatings of Paraloid B-72, Mowilith 20 and Laropal A 81 each produced surfaces on both clean and oxidized coupons with a Moiré pattern; and the coatings of Beva 371b produced a whitish, matte coating in both cases.

Adhering oil paint fragments

Paint fragments with an approximate area of 3 mm x 2 mm were removed from the paint drawdown, which had been applied to a sheet of Melinex® (100 microns thick); using a scalpel with a number 11 blade (see Appendix VI, Equipment & Suppliers).

Three paint fragments were placed on the top surface of each coupon (the top surface carried the engraved number of the coupon). Immediately afterwards, the consolidant solution was applied using a fine sable-haired brush (see Appendix VI, Equipment & Suppliers). Excess consolidant in the brush was first drained off onto a sheet of Melinex® and then the consolidant was introduced on each paint fragment by touching the underside of the fragment with the brush such that the liquid ran under the

fragment and was deposited at the paint/copper interface. This method ensured that the fragments were not encapsulated in consolidant; rather it was delivered to the interface only.

While adhering the fragments, differences were noticed depending on the type of solution and on the condition of the surface (cleaned or oxidized): Paraloid B-72, Mowilith 20 and Beva 371b travelled under the paint fragments on clean copper surfaces much easier than on the oxidized coupons; and as for Laropal A 81 the opposite occurred.

Step 5. Accelerated ageing in a climatic chamber

Coupons destined to go into the climatic chamber were placed on a glass support (in the PROME guidelines [34], a Plexiglas® support is recommended) at an inclination of approximately 30º to the vertical, with the aim of avoiding deposition of dust and dirt and the accumulation of water on the surfaces.

The ageing cycle was programmed into the climatic chamber (see Appendix VI, Equipment & Supplies), to provide two main periods with different T and RH conditions (see Table V.4), and also a period of transition between each one (not referred in the PROMET guidelines regarding this method of ageing [32]), due to the fact that the chamber changes the T and HR gradually, not abruptly, thus requiring time to stabilize. Therefore, two transition periods of 1 hour of duration were included in the ageing cycles to ensure that the conditions inside the chamber would be at the desired values when the main periods began. According to the same logic and for the same reasons, there was also the need to program a first initial segment (segment 0) when starting the program. As a result, the actual ageing program put into practice consisted of 30 cycles of 24h, each divided in 4 segments plus the initial one (0), as described below in Table V.4.

Table V.5 – Ageing program put into practice in detail

Segment no.	Type of segment	Set Value for Temperature (ºC)	Set Value for Relative Humidity (%)	Segment duration (h)
0	Initial	23	55	-
1	Main	23	55	7
2	Transition	35	90	1
3	Main	35	90	15
4	Transition	23	55	1

When segment number 4 ended, the chamber would go back to the beginning (segment number 1), thus repeating the sequence 29 times until the ageing program was completed.

Step 6. Control group in lab environment

The coupons destined to remain in the paintings laboratory at ambient conditions (in a monitored environment) were placed on an inclined support similar to that used for the climatic chamber, but built with polyethylene fluted sheets (see Appendix VI, Equipment & Suppliers). A tent made of thin

Melinex® (12 microns thickness) was placed over the coupons to avoid dust accumulation on the surfaces of the coupons.

Appendix V.5 – Instruments description

- **RBS**

RBS measurements were done in the *Small* chamber located at the channeling experimental beam line of the 2.5MV Van de Graaff accelerator. A 2MeV alpha particle beam was used, with the approximate dimensions of 1x1 mm^2. The current was kept at 0.4-0.6 nA. The chamber is equipped with three particle detectors, which acquire the three spectra simultaneously for the same sample: RBS1, with an angle of +165°; RBS2, with an angle of -140°; and ERD, with an angle of -165°. Measurements were done at normal incidence and at 10º with the beam direction. Spectra were fitted using WiNDF software. Since no detailed composition of each coating was known based on the literature, the fits were done assuming a chemical composition consisting of $C_5H_8O_2$ for every one.

- **SEM/EDS**

A HR-FESEM Hitachi SU-70 Ultra-High Resolution Analytical Scanning Electron Microscope was used with a SE (secondary electron) detector coupled with a Peltier cooled B-U Bruker QUANTAX 400 EDS spectrometer. Samples were covered with a layer of carbon. The elemental maps were acquired with a voltage of 15.0Kv (high voltage).

Appendix V.6 – RBS analysis results

The coupons were placed in the RBS sample holder with their front surfaces facing outwards, and then put inside a vacuum chamber. Depending on the results obtained during the measurements, one, two, or three different areas of each coupon were analysed. The spectra presented below are those recorded with the ERD detector. The black arrow in all the figures indicates the expected position for the copper at the surface, without any coating.

Coupon 21 - B-72 (cleaned coupon) (Fig. V.2)

No. of analysed areas, measurements and θ		
Area 1	Measurement 1 (black line)	θ = -10º
Area 2	Measurement 2 (red line)	θ = -10º
Area 3	Measurement 3 (green line)	θ = 0º

Measurement 1 exhibited an oddly high amount of Cu diffused towards the surface; therefore, two more measurements were performed for comparison. Both detected the diffusion of Cu from the substrate up to the surface of the polymeric film. It is concluded that the first measurement probably caught an area with no film, thus reading the copper surface directly and explaining the high amount of Cu.

Coupon 22 –B-72 (oxidized coupon) (Fig. V.3)

No. of analysed areas, measurements and θ		
Area 1	Measurement 1 (green line)	θ = -10º

The spectrum shows a very poorly defined area of film thickness with no significant Cu diffusion in it, so no conclusions regarding it can be drawn in this case. An explanation for this would be the irregular surface of the film (roughened/with bubbles).

Coupon 23 – Mowilith 20 (cleaned coupon) (Fig. V.4)

No. of analysed areas, measurements and θ		
Area 1	Measurement 1 (green line)	θ = -10º

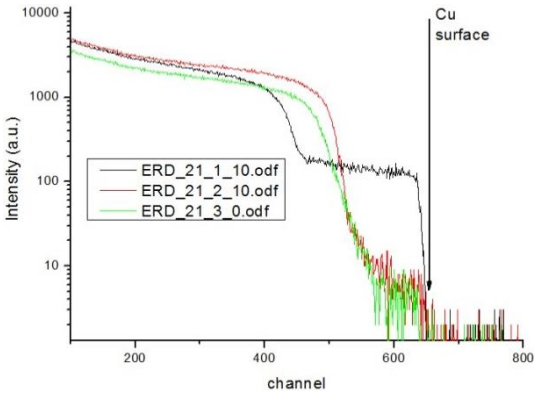


Figure V.2 – RBS spectrum for coupon 21.

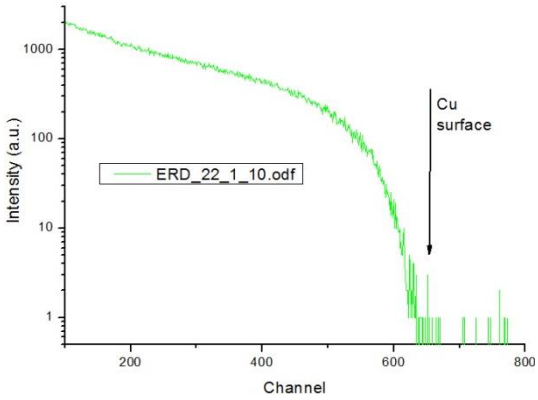


Figure V.3 – RBS spectrum for coupon 22.

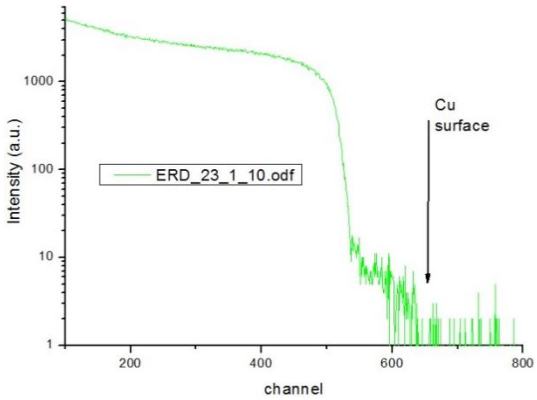


Figure V.4 – RBS spectrum for coupon 23.

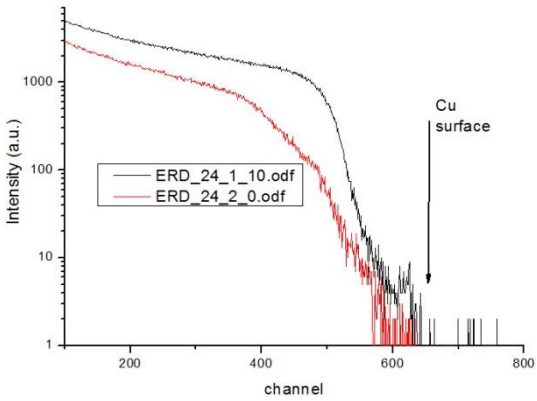


Figure V.5 – RBS spectrum for coupon 24.

The spectrum indicates Cu diffusion from the substrate up to the surface of the polymeric film, with a well-defined film thickness area.

Coupon 24 – Mowilith 20 (oxidized coupon) (Fig.V.5)

No. of analysed areas, measurements and θ		
Area 1	Measurement 1 (black line)	θ = -10º
Area 2	Measurement 2 (red line)	θ = 0º

Both spectra seem to have some Cu diffused near the surface of the polymer. However, the thickness areas are poorly defined, making it difficult to draw very concise conclusions.

Coupon 25 – Laropal A81 (cleaned coupon) (Fig.V.6)

No. of analysed areas, measurements and θ		
Area 1	Measurement 1 (black line)	θ = 0º
Area 2	Measurement 2 (red line)	θ = -10º

Both spectra are very similar. The film is so thin that is below the limit of the technique in this configuration. Although there are other possibilities as: the film was completely eroded in the initial stage of the analysis, thus resulting in spectra with a direct reading of the Cu substrate; measurements done in an area where there was no film. No conclusions regarding Cu diffusion can be made in this case.

Coupon 26 – Laropal A81 (oxidized coupon) (Fig.V.7)

No. of analysed areas, measurements and θ		
Area 1	Measurement 1 (black line)	θ = -10º
Area 2	Measurement 2 (red line)	θ = 0º

Both spectra are very similar to the ones acquired in coupon no. 25. Therefore, no conclusions regarding Cu diffusion in this coupon can be made.

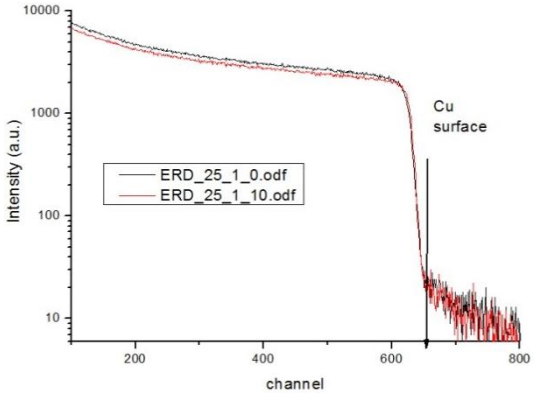


Figure V.6 – RBS spectrum for coupon 25.

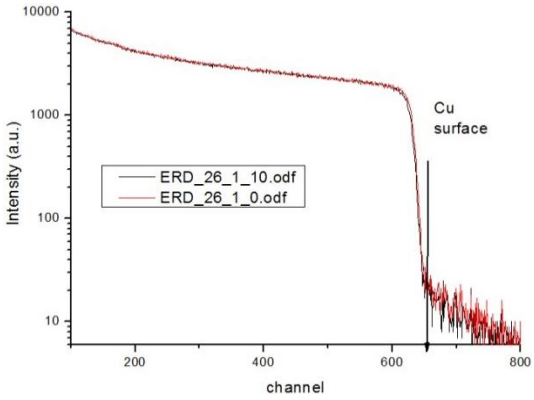


Figure V.7 – RBS spectrum for coupon 26.

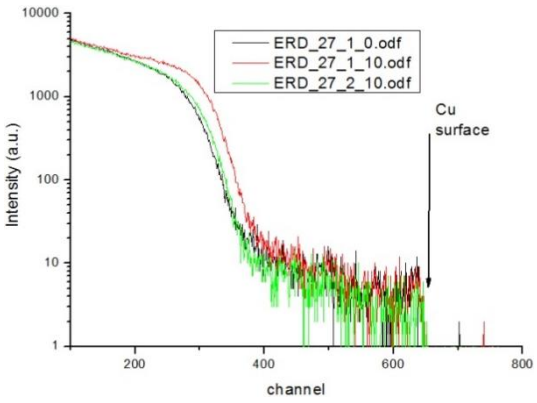


Figure V.8 – RBS spectrum for coupon 27.

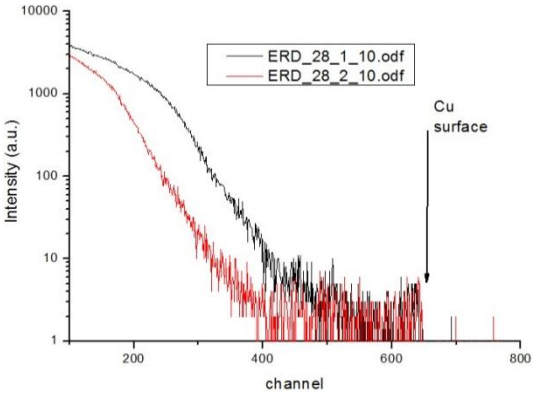


Figure V.9 – RBS spectrum for coupon 28.

Coupon 27 – Beva 371b (cleaned coupon) (Fig. V.8)

No. of analysed areas, measurements and θ		
Area 1	Measurement 1 (black line)	θ = 0º
	Measurement 2 (red line)	θ = -10º
Area 2	Measurement 3 (green line)	θ = -10º

Measurements 1 and 2, from Area 1, detected diffused Cu at the surface of the polymeric film. From the first measurement (black line) to the second (red line) a shift towards higher channels occurred, indicating that the film became thinner. This decreasing thickness in the same spot can indicate that the RBS beam eroded the film during analysis, but not completely, since the second measurement still shows some thickness. In order to verify this hypothesis, a third measurement was acquired (Area 2, green line). The resulting spectrum is very similar to that obtained for measurement 1, thus confirming the theory of beam damage.

Coupon 28 – Beva 371b (oxidized coupon) (Fig. V.9)

No. of analysed areas, measurements and θ		
Area 1	Measurement 1 (green line)	θ = -10º

The spectrum shows a very poorly defined area of film thickness with no significant Cu diffusion in it, so no conclusions regarding it can be drawn in this case. An explanation for this would be the irregular surface of the film (roughened/with bubbles).

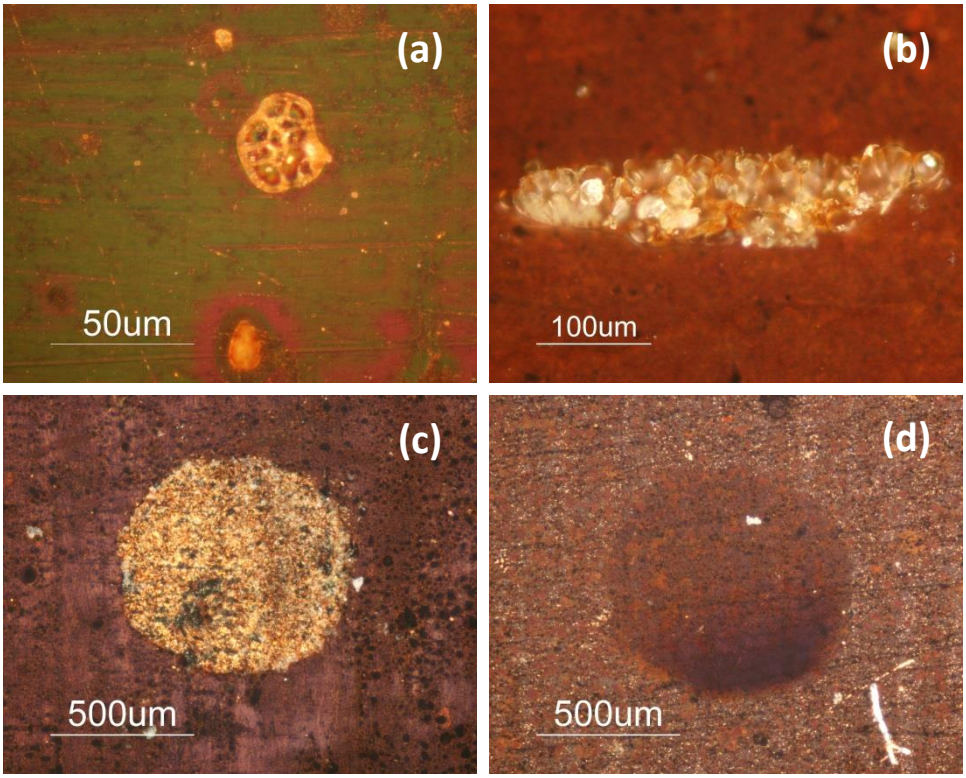


Figure V.10 – Examples of RBS analysed areas observed under OM with normal reflected light: Details: (a) coupon 21 (x500); (b) coupon 24 (x200); Overall views: (c) coupon 22 (x50); (d) coupon 28 (x50). Note the presence of bubbles in (a) and (b); and the evident alteration of the film surface in the rounded areas of analysis in (c) and (d).

Appendix V.7 – SEM/EDS analysis results

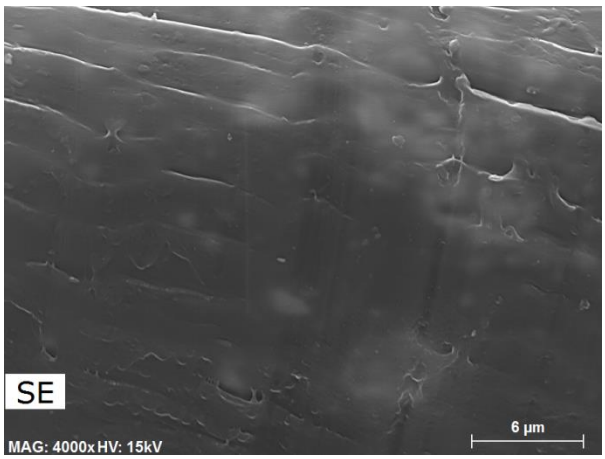


Figure V.11 – SE image of B-72 film on cleaned copper (Coupon 21).

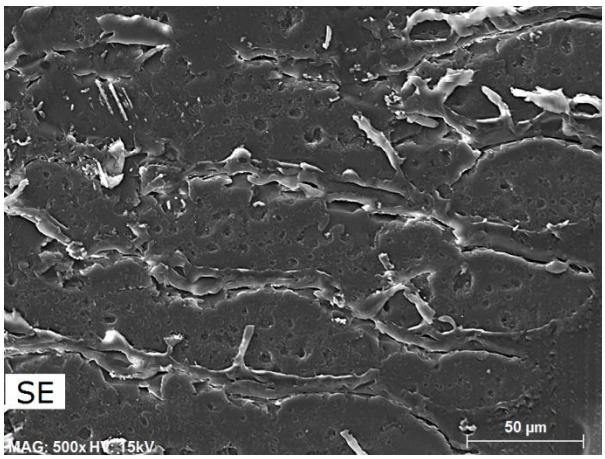


Figure V.12 – SE image of B-72 film on oxidized copper (Coupon 22).

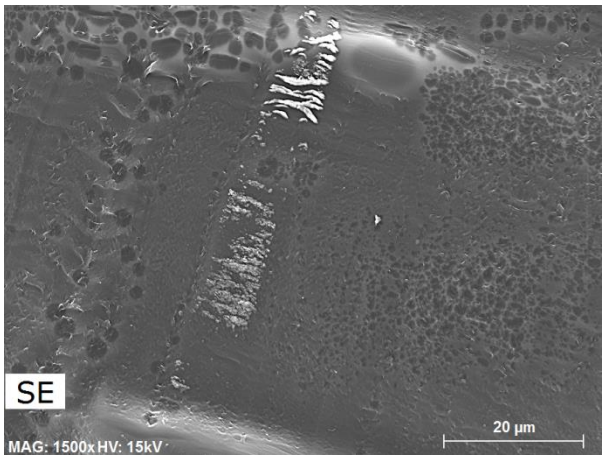


Figure V.13 – SE image of Mowilith 20 on cleaned copper (Coupon 23).

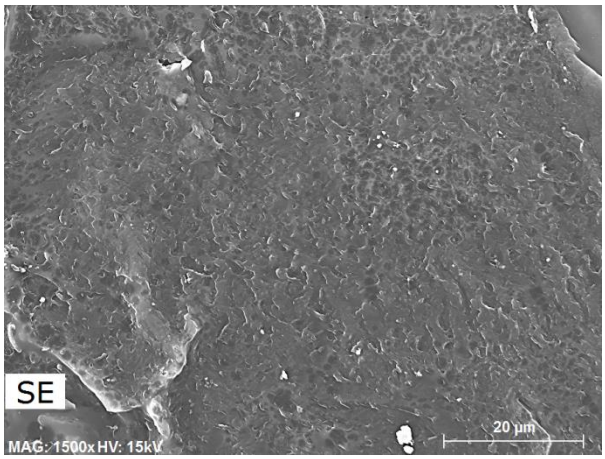


Figure V.14 – SE image of Mowilith 20 on oxidized copper (Coupon 24).

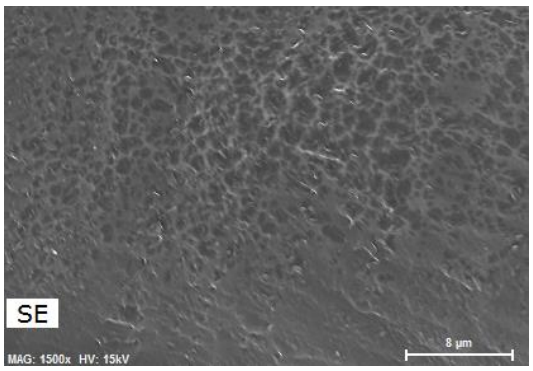


Figure V.15 – SE image of Mowilith 20 on cleaned copper (Coupon 23), at a higher magnification.

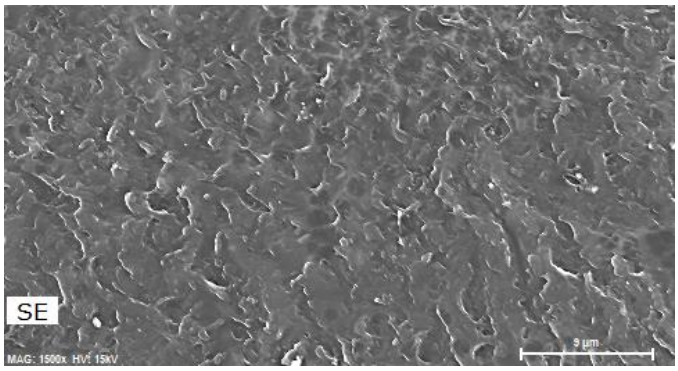


Figure V.16 – SE image of Mowilith 20 on oxidized copper (Coupon 24), at a higher magnification.

Appendix VI – Equipment and Suppliers

Equipment

- **Dremel machine:** Dremel® 300-25;
- **Kiln/Oven:** Memmert GmbH + Co.KG. Memmert; type ULE 400 with 230 V- 6.1 A 50/60 Hz 1400;
- **Climatic chamber:** Aralab FITOCLIMA 300 EC20;
- **Scanner:** hp scanjet 8200 flatbed scanner.

Suppliers

Product	Supplier	Date of Receipt
Copper plate 99% copper; 0.7mm thickness	Jewellry Store Lima & Teixeira, Lisbon, Portugal Tel. 21 847 53 91	Purchased 2015
Jewellers saw blades 3/0, Glardon® Vallorbe	Jewellry Store Lima & Teixeira, Lisbon, Portugal Tel. 21 847 53 91	Purchased 2015
Micro-mesh polishing clothes Grit: 6000;8000;12000	SONUS	FCT-PNT Stock 2014
Pyrex glass container Round Pyrex® glass bakeware with lid, 1 L	Home and decoration store Pollux, Lisbon, Portugal https://www.pollux.pt/	Purchased 2015
Fine sable-haired brush Winsor & Newton Cotman Watercolour Round III Series	FCT-PNT Stock	FCT-PNT Stock
Polyester film Melinex® 12 μm; 100 μm thickness	pel (Preservation Equipment Ltd.) https://www.preservationequipment.com/	FCT-PNT Stock
Polyethylene fluted sheets Coroplast®, 0.5 cm thickness	pel (Preservation Equipment Ltd.) https://www.preservationequipment.com/	FCT-PNT Stock
BEVA® 371b (Gustav Berger's Original Formula® 371, 40% solution)	Kremer Pigmente GmbH & Co. KG www.kremer-pigmente.de	FCT-PNT Stock 2013
Laropal® A 81	Kremer Pigmente GmbH & Co. KG www.kremer-pigmente.de	FCT-PNT Stock
Mowilith 20	Kremer Pigmente GmbH & Co. KG www.kremer-pigmente.de	FCT-PNT Stock
Paraloid™ B-44	Kremer Pigmente GmbH & Co. KG www.kremer-pigmente.de	FCT-PNT Stock
Paraloid™ B-67	Kremer Pigmente GmbH & Co. KG www.kremer-pigmente.de	FCT-PNT Stock
Paraloid™ B-72	Kremer Pigmente GmbH & Co. KG www.kremer-pigmente.de	FCT-PNT Stock
Regalrez® 1094	Kremer Pigmente GmbH & Co. KG www.kremer-pigmente.de	FCT-PNT Stock